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Feasibility of Primary Copper Smelter Weak Sulfur Dioxide Stream Control

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16. ABSTRACT

The major source of uncontrolled emissions of SO_2 from primary copper smelters in the U.S. is the reverberatory furnace because gas strength is too low for direct processing in a sulfuric acid plant, the accepted control approach in this industry. Systems and techniques that experience indicates, either singly or in combination, can be used to control weak SO_2 emissions from copper smelters are identified, analyzed and discussed.

Two overall approaches to weak SO_2 stream control are (1) increasing the concentration of SO_2 to a range where it is feasible to produce sulfuric acid or other useable byproducts or (2) neutralizing the effluent as a waste product. Process modifications to minimize the use of air such as in-leakage control and oxygen enrichment can significantly increase SO_2 concentration. The use of add on systems to concentrate the weak SO_2 such as the magnesium oxide, ammonia and citrate systems have demonstrated applicability. The lime or limestone neutralization process where forced oxidation is used to produce gypsum has been demonstrated as an approach to producing a "throw away" product. Coal reduction to sulfur also shows sufficient promise for serious consideration. Product markets are discussed.

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by

I.J. Weisenberg
T. Archer
F.M. Winkler
T.J. Browder
A. Prem
Pacific Environmental Services, Inc.
Santa Monica, California 90404

Contract No. 68-03-2398

Project Officer

John O. Burckle
Industrial Pollution Control Division
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

The primary nonferrous metals industry is the second largest stationary source category of SO_2 emissions, after fuel combustion in utility and industrial boilers. Uncontrolled SO_2 emissions from primary copper smelting are approximately equivalent to the quantity that would be generated by eight to nine 1000 megawatt power plants using 4% sulfur coal.

In current domestic practice, strong sulfur dioxide gas streams are controlled by metallurgical acid plants at all except two smelters where they are uncontrolled. The weak sulfur dioxide streams, i.e., those not amenable to processing in the acid plants, are currently uncontrolled for lack of applicable control technology. This report explores the technical feasibility of a number of approaches either under development or employed at full scale in smelters abroad.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

PREFACE

Weak SO_2 streams from copper smelters are generated from multihearth roasters and reverberatory furnaces. New copper smelters would only emit weak SO_2 streams from reverberatory furnaces. The objective of this report is to present all possible ways, procedures and systems available for SO_2 control.

Contractually a task report is required for each of the four major tasks: (1) Operating Conditions Determination; (2) Processing Technique Modification; (3) Oxygen Enrichment; and (4) Concentration and Neutralization Systems. These have been combined in this volume. Detailed analyses and supporting data have been included in an extensive appendix.

This report was submitted in fulfillment of EPA Contract 68-03-2398 by Pacific Environmental Services, Inc. under the sponsorship of the U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Industrial Pollution Control Division, Metals and Inorganic Chemicals Branch, Cincinnati, Ohio.

ABSTRACT

The major source of uncontrolled emissions of SO_2 from primary smelters in the United States is the reverberatory furnace. Approximately 22 percent of the sulfur input to copper smelters is emitted from the reverberatory furnace. Average emissions of SO_2 range from 0.4 percent to 1.5 percent by volume which is too low for processing in a sulfuric acid plant, the accepted control approach in this industry. The primary objective of this study is to identify systems and techniques that experience indicates, either singly or in combination, can be used to control weak SO_2 emissions from copper smelter reverberatory furnaces. In some cases, multihearth roasters also generate weak SO_2 streams and their control is a secondary objective of the study.

There are two overall approaches to the control of weak SO_2 stream emissions. These are to (1) increase the concentration of SO_2 to a range where it is feasible to produce sulfuric acid or other useable by-products, or (2) neutralize the effluent as a waste product. Approaches to weak SO_2 stream control such as processing modifications, oxygen enrichment, and the use of concentration or neutralization systems have been reviewed to identify those having sufficient full-scale or plant size use to qualify them as representing available technology. Detailed composition of reverberatory furnace emissions and operating characteristics were determined to provide a basis for the control approach evaluation.

Construction, operation, and maintenance of the reverberatory furnace can play a major part in the concentration of SO_2 in the offgases. With operating techniques such as sealing of all cracks and openings, close control of internal pressure, reduction of excess burner air and oxygen enrichment, increases in average SO_2 content of 1 percent can be achieved (i.e., from an average of 1.5 to 2.5 percent SO_2). While this

is still not sufficient to allow direct processing in a conventional sulfuric acid plant, it is a sufficient increase over conventional practice to provide significant reduction in subsequent size and complexity of retrofit concentration or neutralization systems. Recent experience by a smelter in Chile has indicated that average SO_2 concentration from a green charge reverberatory furnace can be increased to as high as 5 percent using oxygen enrichment.

Considerable experience has been accumulated in Japan on the lime/limestone gypsum neutralization system using green charge reverberatory furnace offgases. Full-scale plant size experience has also been obtained there on the magnesium oxide regenerative system processing green charge reverberatory furnace offgases. These two systems confirm that control of the copper smelter reverberatory furnace is available as current state-of-the-art. Additional concentration systems that have been operated at plant-scale are the ammonia system used for several years at a copper-lead smelter and a coal reduction process with sulfur as the product. The modified cold water concentration system has been successfully applied at full-scale, and pilot plant experience, with smelter gases indicates this system can operate at concentrations from 0.5 to 5 percent SO_2 using citrate as the buffering agent.

An alternate approach modifying a conventional sulfuric acid plant has been reviewed to indicate that even with the low SO_2 concentration currently being emitted from U.S. reverberatory furnaces, it is possible to process this gas directly to produce sulfuric acid. This can be done with a minimum of energy expenditure by a proposed technique even though actual full-scale experience was obtained using the high energy approach.

A study of the uses or disposal of control system products was conducted as an aid to evaluation. The neutralization system with the most disposable product is one that produces gypsum. While it may not be possible for this product to be sold in the U.S., its disposal by landfill or settling pond does not introduce any additional pollution problems. A review of the sulfuric acid market indicates that this market will be supplied by utilities and refinery by-product acid as well, thereby maintaining a very competitive situation. However, the smelters can price their acid down to a cost considering shipping equivalent to that for neutralization on-site. Reduction of the sulfur dioxide to sulfur would provide a readily storable product; however, the complexity of providing a reducing agent tends to inhibit this approach. Coal is the most logical reducing agent which could be used either directly or indirectly as a source of reducing gas with the consequent complexity of an additional system.

While each individual smelter with a reverberatory furnace or multihearth roaster must consider the various techniques available to determine the best local approach, it is clear that existing techniques either singly or in combination can be used to control copper smelter reverberatory furnace SO_2 emissions.

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SECTION 1

SUMMARY

Most of the primary copper ores in the world are obtained from sulfides. The vast majority of the extraction techniques that are used involve pyrometallurgy, usually starting with copper concentrates. Since the primary objective is to separate the copper from the sulfur containing materials, large quantities of sulfur dioxide (SO_2) are generated in all copper smelters.

The typical or conventional copper smelter processes the concentrates with suitable fluxes initially in a roaster, followed by a reverberatory furnace, and then a converter. The roaster removes the easily removable atom of sulfur to adjust the copper to sulfur ratio for further processing in the reverberatory furnace which produces a material called matte. The matte generally contains approximately 40 percent copper. The matte is then further refined in a converter which first reduces and then oxidizes it to produce approximately 99 percent blister copper. The blister copper is then fire refined, cast into anodes and finally electrolytically refined to meet extreme purity requirements.

The three major pyrometallurgical steps generate considerable quantities of sulfur dioxide sufficient to classify smelters as the second largest SO_2 emission source in the U.S. Multihearth roasters will usually generate gases containing approximately 4 percent SO_2, although older units, which may contain considerable leaks, can generate gases as low as 2 percent. Fluid-bed roasters will produce an 8 percent average SO_2 concentration. Sulfur dioxide offgas streams from fluid-bed roasters tend to be sufficiently high in concentration to process in a sulfuric acid plant. Current multihearth roaster SO_2 offgas streams are usually too low in SO_2 concentration for effective acid plant processing.

The major source of uncontrolled emissions of SO_2 from primary copper smelters in the United States is the reverberatory furnace. Sulfur dioxide emitted from the reverberatory furnace averages 22 percent (by weight) of the total sulfur entering the smelter, but can be as high as 34 percent for green charge or as low as 9 percent for calcine charge produced with a fluid-bed roaster. Average emissions of SO_2 from reverberatory furnaces range from 0.5 to 1.5 percent by volume. This volume is too low for processing in a conventional sulfuric acid plant, which is the accepted control approach in this industry. Approximately 25 reverberatory furnaces are presently in operation in the U.S. and can be expected to continue for several decades because they offer many operational advantages.

The converters will generate offgases containing from 3-1/2 to 6 percent SO_2 depending upon how these gases are collected and depending upon the blowing cycle. Because of the higher concentration of the gases leaving the converters, it has been generally conventional practice in the U.S. industry to collect these gases and pass them to a sulfuric acid plant. In all cases except two, a sulfuric acid plant is used to convert the SO_2 to H_2SO_4 which is generally then sold or used internally in other operations around the smelter or mine.

It is the objective of this study to examine all of the possible techniques that could be used for controlling SO_2 from the reverberatory furnace and other low SO_2 content streams found in copper smelters. The techniques included are those that can be considered "available" on the basis of demonstrated experience either on full-scale operating equipment or on plant size systems in other industries. Process modifications to increase SO_2 concentration and the use of auxiliary systems for concentration or neutralization are reviewed. It is clear that all techniques presented may not be applicable to any particular smelter. However, with an overview of all possible practical techniques, the optimum approach or combination of approaches for the specific local situation can more readily be selected.

The new source performance standard for copper, lead, and zinc smelters exempted the reverberatory furnace SO_2 control for those cases where the feed contained quantities of impurities such as arsenic, lead, and zinc higher than certain specified values. The reason for this is that usually high impurity copper concentrates, i.e. dirty feed, are prepared for smelting by using a preliminary roasting step to control subsequent furnace and converter processing. At the time of promulgation, in 1976, information on the roaster/reverberatory, roaster/electric furnace, or green charge electric furnace had confirmed capability of providing a suitable matte for converter processing with impurities. Since the NSPS assumed that only flash smelters or electric furnaces would be used for new smelters, it was necessary to allow use of a reverberatory furnace for dirty feeds in those locations where electric power was not economically available. Sulfur dioxide control from the reverberatory furnace had not been demonstrated sufficiently at that time. This study also includes a review of the design approaches for providing SO_2 for a new smelter.

Problems associated with controlling SO_2 in existing smelters are somewhat different than those in new smelters. The condition of the equipment can be considerably different in the old smelters resulting in dilution effects and lower SO_2 concentrations in the offgases. In addition, installation of new control equipment may be more difficult in the case of the older smelters than with a new design. Furthermore, new smelters seem to be using flash smelting or similar systems which result in higher concentrations of SO_2 in the offgases making them amenable to direct processing in a sulfuric acid plant.

The offgas stream blending technique study was conducted by establishing a series of equipment and operating scenarios primarily related to a new green field smelter. The review of methods for controlling the reverberatory furnace can, in most cases, be retrofitted to existing smelters. In some cases, the blending techniques can also be retrofitted.

The use of the blending technique for retrofit was not completely studied for application to existing smelters because site specific conditions strongly affect the utility of this technique. For example, the characteristics of the offgas streams from equipment of similar design can vary from smelter to smelter, or even within the same smelter with time, depending on the feed sulfur content variations. Also, the condition of the operating equipment will affect the input leakage and result in reduction in SO_2 concentration for the older equipment.

The review of the operation of a sulfuric acid plant processing offgases from a copper smelter was also conducted to determine the most optimum operating conditions. It was found that, in some cases, even when SO_2 concentration is high enough for direct processing, combining an FGD system with an acid plant will tend to reduce the overall load and design requirements on an acid plant for a copper smelter when compared to using only a sulfuric acid plant for control. Acid plant equipment size is reduced by reducing the volume flow rate and the efficiency increased by raising the SO_2 concentration. For example, when a magnesium oxide FGD system is used where 10 to 13 percent SO_2 concentration offgas is produced, overall control system size (and cost) is greater than when a citrate system with over 90 percent generated SO_2 gas is used.

Detailed composition of the reverberatory furnace emissions and its operating characteristics to provide a basis for SO_2 control system design are presented. The factors influencing sulfur dioxide emissions from within the furnace were determined. The effects of operating practices, firing rate, and operating pressure were investigated. Physical configuration of the furnace and sources of dilution were also defined.

The sulfur dioxide generation within the reverberatory furnace can fluctuate from as high as 5.0 percent to as low as 0.1 percent over a period of time. It has been found that the major factors influencing these fluctuations are rate and frequency of furnace charging and charge composition. As the charge enters the furnace, there is a very rapid evolution of sulfur dioxide which then tapers off until the next charge is introduced. The large volume of gas within the furnace tends to reduce the amplitude of these fluctuations, but they can still be detected in the emission measurements. Charge composition controls the availability of sulfur to form sulfur dioxide under furnace operating conditions.

Potential metallurgical processing and equipment operating techniques were investigated that could be used or modified either to (1) increase the SO_2 concentration and reduce offgas volumes to facilitate processing, or (2) to decrease SO_2 concentration to a sufficiently low level to allow either neutralization or direct emissions to the atmosphere with no controls. The use of roasters to produce calcine versus the direct processing of "green" charge indicated that the choice is somewhat dependent upon metallurgical and energy considerations. With calcine charge obtained by preroasting, the amount of SO_2 generated in the reverberatory furnace can be considerably reduced (e.g., from an average of 1.5 to 0.5 percent) which can be advantageous with some control techniques. A strong SO_2 stream can be obtained from the roaster (particularly fluid-bed roasters), which can facilitate overall smelter offgas control. The SO_2 concentration leaving the reverberatory furnace can be increased by various factors such as preheating air, reduction of burner excess air, closely controlling furnace pressure to just below atmospheric, sealing leakage points, charging more uniformly and consistently, and using oxygen enrichment.

Preheating furnace burner air (required when gas is used for fuel) by indirect heat exchange reduces the amount of fuel which must be burned within the furnace to generate the required smelting heat. As a result, the quantity of air required and the associated nitrogen dilution is reduced. Reduction of burner excess air entering the furnace also results in a reduction in the nitrogen dilution effect. Controlling the furnace pressure to just below atamospheric (e.g., 0.005 to 0.05 inches water column) minimizes the quantity of dilution air that can enter through any leakage point. Sealing of leakage points can materially reduce the dilution and increase the average SO_2 concentration. The more uniformly and consistently the furnace is charged, the less the amplitude of the SO_2 fluctuations, thereby allowing the design capacity of a control system to be minimized.

Considerable work both in the United States and foreign countries on adding oxygen to reverberatory furnaces has been conducted. The general conclusion is that the increase in SO_2 concentration resulting from O_2 enrichment can vary from 0.3 to as high as 16 percentage points. The Caletones smelter in Chile has obtained 5 to 7 percent SO_2 operationally from a green feed reverberatory furnace. In addition, the production rate in the furnace can be considerably increased.

There are at least six different ways of injecting oxygen into the reverberatory furnace. The most successful appears to be with a separate oxy-fuel burner which allows the flame to impinge directly upon the charge banks. Development work has indicated that oxygen lancing is another promising appraoch. Problems with furnace durability have been encountered. However, with careful injection of the oxygen in the proper location, it has been determined that furnace durability per ton of produced copper is not affected. When the furnace is operating at capacity without oxygen enrichment, there is an economic reason for using this technique if additional production is required. In most cases, where the furnace is not required to operate at peak production, the use of oxygen would only be required for pollution control reasons unless possibilities for fuel savings are economically justified.

Flue gas desulfurization systems applicable to the reverberatory furnace were reviewed. The objective of the review was to find full-scale operating experience on specific systems, preferably with a reverberatory furnace, but at least on a full-scale plant such as a utility.

Two systems were found that have been operating on the offgases from a copper smelter reverberatory furnace for at least 2 years. One was a magnesium oxide concentration system that absorbed the SO_2 from the weak stream and regenerated it at a concentration in the 10 to 13 percent range. This is sufficiently high to mix with other gases for direct feeding to a conventional sulfuric acid plant. The second system that has been in operation for approximately 4 years is a nonregenerative lime/limestone system.

This particular system was designed to produce gypsum as a saleable product. Additional systems that were reviewed included ammonia scrubbing, Wellman-Lord, citrate, and the Cominco and Foster Wheeler coal reduction systems. Ammonia scrubbing, citrate, and the Cominco coal reduction processes were used at full or pilot scale on metallurgical plants. None, however, were used directly at full scale to process copper smelter reverberatory furnace offgases.

A comparison study of the differences between utility and reverberatory furnace offgases was conducted to determine if technology could be transferred. With some adjustment in operating conditions there does not appear to be any major technical reason why experience with offgases from utility boilers cannot be applied to reverberatory furnace offgases. In fact, the lime/limestone and magnesium oxide system technology was successfully transferred from power plant to copper smelter reverberatory furnace offgases. Also there appears to be a strong indication that the ammonia and citrate scrubbing and the coal reduction systems with metallurgical gas processing experience can be applied to control SO_2 from reverberatory furnaces as well as other weak SO_2 offgases.

As part of the flue gas desulfurization study, modifications to conventional sulfuric acid plant design were reviewed to determine the applicability of direct processing of the weak furnace offgases without concentratic One system in Japan was successfully used on offgases from copper smelter furnaces but required considerable energy for gas reheat to promote catalytic reaction and refrigeration for water balance. A design study was conducted indicating the potential for using available energy from part of the reverberatory furnace offgas and rejected heat from acid heat exchangers. An alternate approach can conserve refrigeration energy by mixing with a source of 98 percent plus acid or oleum, if available, to maintain acid plant water balance.

The potential primary products from SO_2 control systems are sulfur, liquid SO_2, sulfuric acid, and gypsum. Of course, these products can be used as termediates to make a very wide range of additional byproducts. Control system by-product markets and disposal were reviewed. The most storable and shipable material is sulfur. It, however, requires a reducing agent to produce, which makes it the most costly. Furthermore, the available reducing agents are usually fuels. The selection was limited to coal because of the energy situation. At least three smelters have used a system with coal reductant to produce sulfur on a full-scale basis with gases from equipment other than reverberatory furnaces. Liquid SO_2 has a very limited market but can be used for producing other products including sulfuric acid. Presently, sulfuric acid is the primary product generated by smelter SO_2 control techniques. The distance which sulfuric acid can be economically transported is limited to 200-1,000 miles. The smelters in the southwest have the greatest disadvantage from this standpoint. Gypsum can be used to make useful products such as wallboard or "thrown-away" as a landfill. Gypsum production eliminates the sludge treating problem associated with some lime/limestone scrubbing systems which do not completely oxidize the product. It is a stable product and could be directly disposed of without creating any water pollution problems.

Additional data on copper smelter pollution control techniques were obtained during a visit to Japan in January 1977. Information from that trip is included in this study. The Japanese are more advanced than the U.S. in SO_2 control of copper smelters. By 1978, the Onahama copper smelter at Iwaki City, Japan, with two conventional green charge reverberatory furnaces, was required to control 99.5 percent of the total input sulfur. In 1977, they were controlling well over 95 percent using either the lime/limestone gypsum or the MgO-sulfuric acid systems for weak SO_2 streams.

It can be concluded from the data included in this study that SO_2 control of the weak offgas stream from a primary copper smelter reverberatory furnace has been demonstrated to be technically feasible using several different approaches or combinations of these techniques. Control of SO_2 can be accomplished by blending of strong and weak gas streams with new or well maintained smelting equipment. Using processing techniques and concentration (FGD) systems maximizes initial stream SO_2 concentration for efficient processing in sulfuric acid plants.

SECTION 2

CONVENTIONAL COPPER SMELTING AND SO_2 CONTROL SYSTEMS

2.1 GENERAL

Conventional practice for the production of blister copper (approximately 99 percent pure copper) from copper sulfide ore concentrates includes three operations:

1. Roasting (optional) to remove a portion of the concentrate sulfur content in multihearth roasters or fluid-bed roasters.
2. Smelting of the concentrate and fluxes in a reverberatory furnace to form slag and copper-bearing matte.
3. Oxidizing the matte in a converter to form blister copper.

Although roasting is a common practice, many smelters throughout the country bypass this process step and charge the concentrates "green" to a reverberatory furnace. Whether a smelter uses a roaster or not is primarily controlled by the copper-to-sulfur ratio in the feed going to the reverberatory furnace as well as impurities in the ore that must be eliminated pyrometallurgically. In the case of a custom smelter where the ratio and impurities may change widely with different ores, a roaster is usually required to control the ratio and subsequent matte grade.

Other "modern" smelting systems are used for copper production today and are discussed in the literature. However, this study concentrates on the copper smelter using a conventional system, namely, roaster, reverberatory furnace, and converters as discussed in subsequent paragraphs.

2.2 ROASTING

2.2.1 PROCESS

A major portion of the sulfur contained in copper concentrates can be removed through the roasting process. This sulfur elimination results in a higher grade matte formed in the reverberatory furnace and subsequently reduces the oxidation load on the converters.

Roasting is often practiced prior to reverberatory smelting. Roasting serves to dry and heat the reverberatory charge by using the exothermic heat from the roasting reactions. Hot roaster calcines require considerably less energy for smelting than cold, wet concentrates. Therefore, roasting results in a considerable fuel saving and an increased smelting rate in the reverberatory furnace. Roasting also increases the copper concentration of the Cu_2S: FeS matte produced during smelting, a factor which decreases the amount of converting subsequently required. Roasting is also performed to regulate the amount of sulfur so that the material can be efficiently melted and matte composition controlled to ensure that certain volatile impurities are eliminated in the converting step.

Sulfur dioxide is a byproduct of roasting. Its concentration in the effluent gases can be high (5 percent SO_2 in new hearth roaster gases, and 8 to 10 percent SO_2 in fluid-bed roaster gases) which can effectively be removed as sulfuric acid.[1] Older hearth roaster systems generally produce a much lower SO_2 concentration gas (1.0 to 2.5 percent) because of input leakage of air.

2.2.2 MULTIHEARTH ROASTERS

The multihearth roaster is a refractory-lined cylindrical vessel, fitted with seven to twelve refractory hearths. Concentrates are fed into the top of the roaster and are raked across each hearth before falling to the next lower level. These rakes are attached to a rotating control shaft. Air for roasting usually enters at the bottom of the roaster and moves up counter-currently against the descending charge and finally, through a top flue.

The roaster is started by heating to a temperature at which the concentrates will be ignited by air. The concentrates, fluxes, and air are then introduced resulting in combustion. Typically, the upper hearths are used for drying and heating, while lower hearths provide ignition and oxidation reactions. Most of the oxidation reactions are exothermic so that once the ignition temperature is reached, the system operates autothermally. The iron sulfides are oxidized to form Fe_2O_3 and Fe_3O_4 preferentially to copper sulfide oxidation. The roasted concentrates (calcines) are then delivered to a smelting furnace. New multihearth roasters can produce an offgas with an average SO_2 concentration of 4 to 5 percent. Older units with greater inleakage of dilution air may range from 1 to 3 percent SO_2 concentration in the offgas. (For a more detailed discussion of multihearth roasters, refer to Appendix A-1.)

2.2.3 FLUID-BED ROASTERS

Fluid-bed roasting involves the autogenous oxidizing of sulfide particles while they are suspended in an evenly distributed stream of air. It is based upon the principle that air blowing through a bed of fine solids tends to support the particles at moderate velocities. These particles may be permanently suspended in an expanded or fluidized bed. The particles are essentially surrounded by air so that rates of gas/solid roasting reactions are high. The reactions that occur are similar to those that take place in multihearth roasters (refer to Appendix A-1).

Figure 2-1 shows a cutaway of a typical fluid-bed roaster. Air is blown into the roaster by means of a tuyere plate at the bottom, and concentrates are added in particulate or slurry form near the top of the roaster. The roasting operation is begun by heating the roaster (usually containing an inert bed of sand or calcines) to the temperature at which the concentrate will ignite by air. Typical temperatures are maintained between 900°F and 1,200°F. The concentrates are then added, slowly at first, to begin the roasting and to make the operation autogenous.

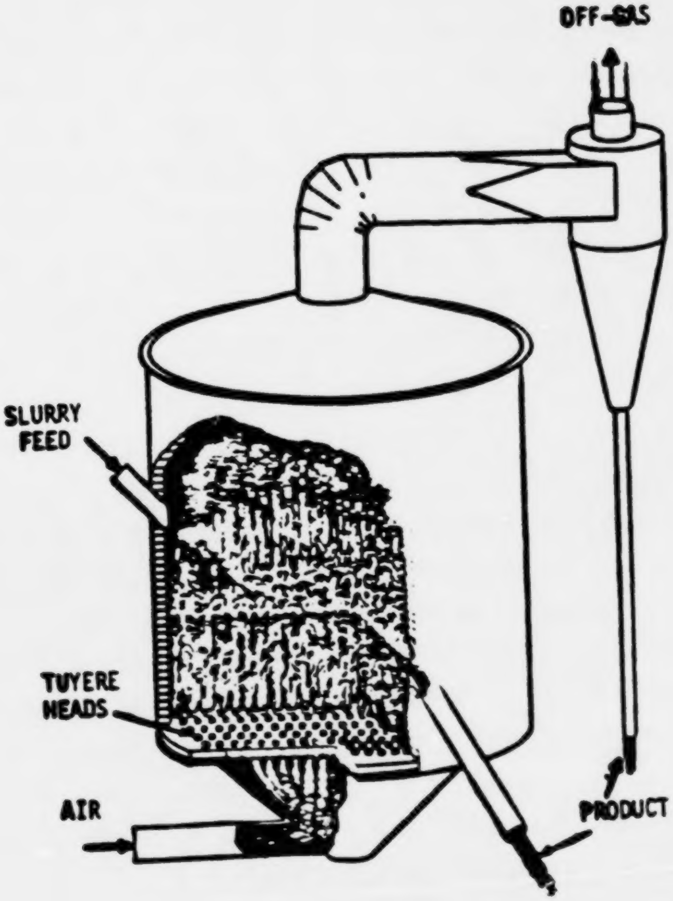

OFF-GAS
SLURRY FEED
TUYERE HEADS
AIR
PRODUCT

Figure 2-1. Typical Fluid-Bed Roaster

Reaction rates within the roaster are rapid, and an important consequence is the high efficiency of oxygen utilization by the roasting reactions. This leads to air requirements only slightly in excess of the stoichiometric amount. Sulfur dioxide concentrations in the effluent roaster gases are considerably higher than those of the multihearth roaster; 9 percent compared to 5 percent (new units). (For a more detailed discussion of the fluid-bed roasters, refer to Appendix A-2.)

Fluid-bed roasters warrant consideration for weak stream SO_2 control since the blending of fluid-bed roaster, reverberatory furnace, and converter offgas has been reported feasible and produces a considerably higher combined SO_2 concentration.[2]

2.3 REVERBERATORY FURNACE

2.3.1 REQUIREMENT FOR CONTROL

The complex nature of the sulfide ores processed in copper smelters result in generation of SO_2 from reverberatory furnaces. The concentration of SO_2 in the offgas may vary from an average of 0.5 to 1.5 percent, values too low for direct processing in a sulfuric acid plant as is currently being done with converter offgases. Thus, no smelter in the U.S. today is controlling reverberatory furnace SO_2 emissions. The study, therefore, concentrated on control technology for this device since over 20 percent of the copper smelter SO_2 emissions can come from this source.

2.3.2 DESIGN

The primary function of the reverberatory furnace is to economically smelt the required copper-bearing charge into a molten mass. The basic advantage of smelting concentrates in the reverberatory furnace is the good extraction to matte of copper and precious metals. The objective of the furnace operation is to produce separate fluid layers of lower specific gravity discardable slag (iron-gangue comprising the top of the bath) and a higher specific gravity matte (consisting theoretically of a mixture of Cu_2S: FeS comprising the lower fluid layer). The matte can be separated by selecting tapping levels. It is then further treated in converters for separation of Cu from the Fe and S. The slag is tapped from the furnace at a higher level and usually discarded.

There are two types of reverberatories currently in use, and they differ principally in the amount of bath and the method of charging.

The first type in use, and still extensively used, is the deep-bath furnace, wherein a molten bath of several feet depth is maintained throughout the furnace, covering the entire bottom. The charge may be admitted to the furnace by (1) dropping through the arch, (2) through retractable or fixed charge guns, (3) discharging through ports in the sidewalls which extend some distance toward the middle of the furnace, or in one instance, (4) through green charge slingers that cover the entire bath in the smelting zone. A calcined charge must be used through charge guns or through arch drop holes in the center or along the furnace sidewalls. Green charge may also be dropped through the arch or introduced through belt slingers. In all cases, every effort is made to distribute the charge on top of the deep molten bath in the smelting area, to expose the largest possible area to the heat from the burners and the arch. Water or air cooled jackets are used in the sidewalls to cool the refractory where the molten bath is in direct contact with the sidewalls.

The second type is the side-charged furnace (refer to Figure 2-2), which is more predominantly in use today and usually has a bath depth of 3 feet or less. Basically, the green or calcined charge is dropped through the arch along the walls to form banks of material that slowly melt, giving sufficient protection to the sidewalls to generally eliminate special cooling requirements. The smelted material forms a liquid bath throughout the center length of the furnace. It is adaptable for either calcine or green feed charging or a combination of both. Typically, feed is gravity-charged into hoppers staggered along each side of the furnace and located above drop holes through an arch, a few inches in from the sidewalls. The hoppers may be fed by calcine car discharge, drag chain distribution of calcine or green feed, or by conveyor belt and tripper car for green feed. As the angle of repose of the charge bank is lesser with calcine charging, the height of the charge pile must be lower or the width of the furnace must be greater than for the bath smelting type. A particular hazard in side charging is the possibility of a portion of the charge bank flowing, caving in, or sloughing into the molten bath and creating a rapid or even explosive reaction between charge and bath with an accompanying boiling and rapid gas evolution, particularly with regard to green or wet feed charging. When using the latter, there have been rare instances where the generated pressure was strong enough to damage the furnace arch and even blowoff portions or sections.

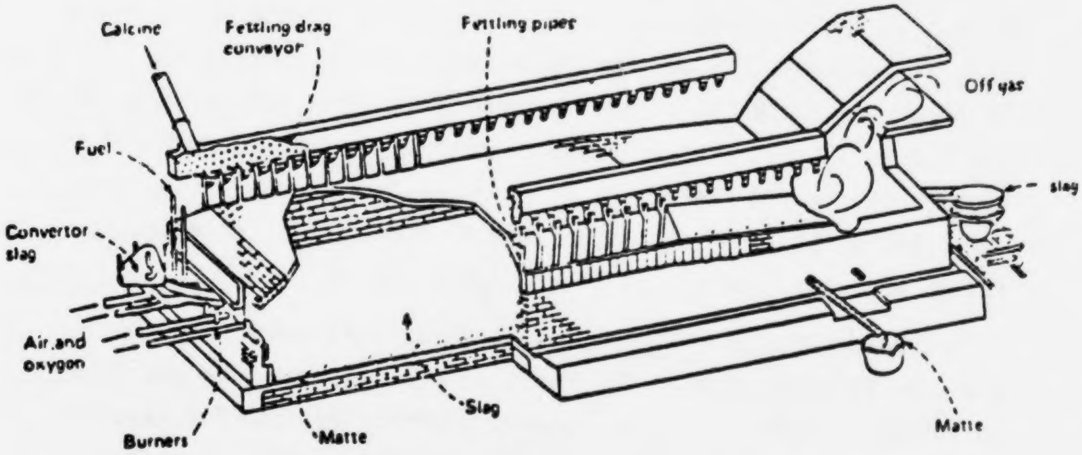

Calcine
Fettling drag conveyor
Fettling pipes
Off gas
Fuel
slag
Convertor slag
Air and oxygen
Burners
Matte
Slag
Matte

Figure 2-2. Side-Charging Calcine by Drag Chains
(Green Feed Can be Fed in Same Manner)

Either sprung or suspended arches may be used in furnaces of either type. If the width of the arch is greater than 25 feet, a suspended type arch must be used as hot brick strengths limit the width of sprung arches.

A description of typical reverberatory furnace, control system design and operation, and a brief history and discussion of smelter energy relationships are included in Appendix B.

2.3.3 FACTORS AFFECTING SO_2 EMISSIONS FROM REVERBERATORY FURNACES

2.3.3.1 Chemistry of Reverberatory Furnace Smelting

An analysis of the chemistry occurring in copper smelting must include a discussion of the input, the reactions being conducted within the equipment, and the output product. Generally, the copper ores considered are the sulfides which can include chalcocite, Cu_2S - 79.8 percent copper; bornite, Cu_5FeS_4 - 63.3 percent copper; tetrahedrite, $Cu_5Sb_2S_7$ - 57.5 percent copper; chalcopyrite, $CuFeS_2$ - 34.5 percent copper; and pyrite, FeS_2 which, though not a copper ore, is frequently associated with copper bearing minerals.[3] Of these, chalcopyrite is the most important ore, particularly in the United States. The percentage of copper in most ores mined is relatively low and therefore, in essentially all cases it is concentrated by various methods, generally flotation. Concentration ratios may vary from 5 to 1 to as high as 40 to 1.

Sulfide ores are mixtures of varying proportions of copper and iron sulfides mixed with acidic or basic gangue. In smelting, advantage is taken of the pronounced affinity of iron for oxygen. Of the commoner metals, iron has the greatest affinity for this element. When a variety of copper ores are melted together they will invariably form cuprous sulfide, Cu_2S. If the proportion of sulfur in the melt exceeds that required to form Cu_2S, the excess will unite with any available iron to form ferrous sulfide, FeS. The two compounds, Cu_2S and FeS, form a series of mixtures with an equilibrium diagram shown in Figure 2-3.

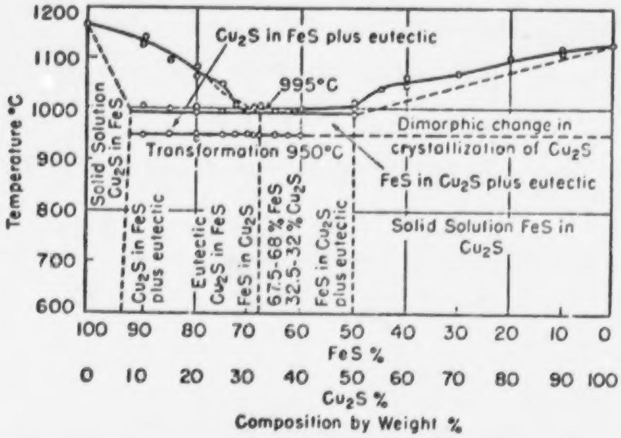


Figure 2-3. Equilibrium Diagram CU_2S-FeS[1]

In copper ore smelting the metallurgist aims at producing mixtures of Cu_2S and FeS containing anywhere from 19 to 45 percent copper (equivalent to 23.5 to 56 percent Cu_2S).[4] These mixtures are known as mattes. They invariably contain small amounts of other sulfides such as PbS and ZnS as well as appreciable proportions of magnetite, Fe_3O_4, wustite FeO, and on occasion, free iron.

Primary reactions occurring during copper smelting including roasting, smelting and converting, are as follows:

Roasting: $2\,FeS + 3\,O_2 \longrightarrow 2\,FeO + 2\,SO_2$

Smelting: $FeS_2 + O_2 \longrightarrow FeS + SO_2$

$CuFeS_2 + O_2 \longrightarrow FeS + Cu_2S + SO_2$

Converting: Slag Blow

$$2\ FeS + 3\ O_2 \rightarrow 2\ FeO + 2\ SO_2$$

Finish Blow

$$2\ Cu_2S + 3\ O_2 \rightarrow 2\ Cu_2O + 2\ SO_2$$

$$2\ Cu_2O + Cu_2S \rightarrow 6\ Cu + SO_2$$

$$Cu_2S + O_2 \longrightarrow 2\ Cu + SO_2$$

The actual chemistry occurring within the pyrometallurgical equipment can be quite complex. Additional reactions occur in all steps, but the aforementioned process above represents the major objectives to produce copper from common ore mixtures.

Most reverberatory furnaces are operated with excess air. However, if there are areas within the furnace where the atmosphere is either reducing or neutral (no oxidation), the sulfur in combination with the copper in excess of that required by the compound Cu_2S will be expelled by volatilization. The resulting cuprous sulfide is rather stable and will fuse without decomposing. Thus, covellite or cupric sulfide, CuS, when heated to a high temperature in the absence of air will decompose according to the equation:

$$2\ CuS \longrightarrow Cu_2S + S$$

yielding molten cuprous sulfide and volatized sulfur. In practice, this sulfur is carried away with other gaseous products of combustion until it comes in contact with air, when it is oxidized to SO_2. Similarly, when iron sulfides are heated in an atmosphere which is not oxidizing all excess sulfur required by the compound, FeS will expel by volatilization. Then, the resulting stable ferrous sulfide will fuse without decomposing.

Iron which does not enter the matte as sulfide is oxidized to FeO and, together with silicate forming elements, unites with the silicate to form a complex fusable material called slag. Usually from 0.3 to 0.55 percent copper is still found in this material and may be lost or saved for further processing. The various fluxes added to the ore charge make the slag composition fusable and fluid in the furnace. This aids in maintaining copper in the matte phase and separation of matte from slag.

Magnetite (Fe_3O_4) may be formed in roasters, converters, or the furnace and introduced during reverberatory smelting. Magnetite produces problems in inhibiting the separation of slag and matte in the furnace as well as causing buildup of the furnace bottom. FeS, when present in the charge, tends to provide reducing conditions which suppress magnetite formation. Also, a highly siliceous slag will tend to minimize its formation; however, this tends to produce a lower grade matte. Raising the temperature of the matte will also minimize magnetite formation.

The products of sulfide ore smelting are matte, slag, dust, fume, and gases. Slag is the product of a reaction between the gangue of the ore and the fluxes introduced with the charge. Dust results from agitation within the furnace. The fume and gases are formed by the chemical reactions within the furnace. Those concentrates with easily volatilized ("dirty") materials, usually heavy metal sulfides, will form fumes which are smaller particles than dusts.

Reverberatory furnace flue gases typically may contain the following:

N_2	72 - 76	percent
CO_2	10 - 17	percent
CO	0.0 - 0.1	percent
O_2	0.5 - 6.0	percent
H_2O	4.0 - 10.0	percent
SO_2	0.5 - 2.0	percent

The amounts of CO_2 and H_2O will depend upon the fuel used and the amount of moisture in the charge; the SO_2 content will depend upon the sulfur elimination from the charge. A large part of the free oxygen may be due to leakage of air through charging holes and other openings in the furnace. These gases will leave the furnace at a temperature of 1,800° to 2,300°F.

The precious metals, gold and silver, contained in the charge are included in the matte when it is withdrawn from the furnace. Composition of various mattes varies from 23 to 44 percent iron, 23 to 27 percent sulfur and 24 to over 50 percent copper.[5]

In practice the sulfur divides itself primarily between the matte and the gases with some going to the slag. That in the matte forms Cu_2S and FeS; that in the gases burns mostly to SO_2. Generally, the sulfur which volatilizes and burns to SO_2 varies from 15 to 30 percent of the total sulfur charged.

The dust generated by the furnace will depend upon the fineness of the particles in the charge, the type of furnace, the method of charging, and many other factors. Fume (material which has been volatilized or sublimed and then condensed when the gases cool) may be a large portion of the dust. The most important constituents found as fume in copper smelters are: (1) the lower volatile oxides of arsenic and antimony (As_2O_3, and Sb_2O_3); (2) oxides of other volatile metals such as PbO and ZnO; (3) condensed water vapor; and (4) sulfuric acid and sulfates. Sulfur trioxide may be formed from oxidation of SO_2 and the SO_3 combined with water vapor to form droplets of sulfuric acid, or it may be combined with certain basic oxides, notably ZnO, to form $ZnSO_4$.

2.3.3.2 Weak Sulfur Dioxide Evolution and Influencing Factors

Figure 2-4 shows a series of SO_2 versus time curves for three reverberatory furnaces at three smelters. While the differences in amplitude can be explained by "available" sulfur present (refer to Section 2.3.3.3), the peaks occur immediately after

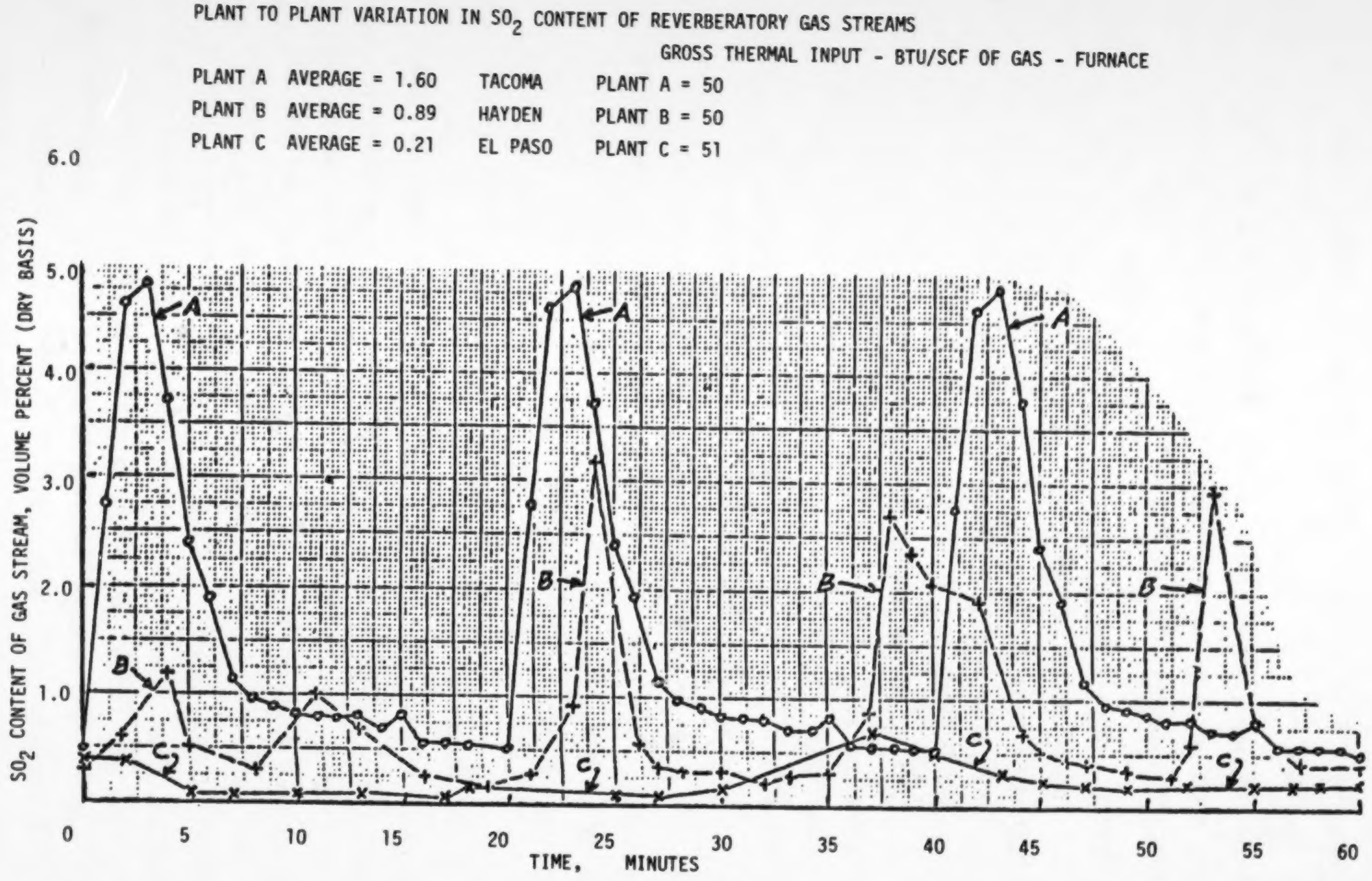


Figure 2-4. SO_2 Emissions Versus Time From Three Different Reverberatory Furnaces

dropping the charge; this cycle is directly related to the charging cycle. Figure 2-5 is a trace showing SO_2 versus time for one smelter in Japan.

There are many factors that affect the SO_2 evolution with time from a copper smelter reverberatory furnace. The following major factors influence SO_2 evolution:

- Charge composition
- Calcine or green charge
- Method of charging
    - Side charge (wall or roof)
    - Top charge
    - Bath charge
    - Continuous or intermittent charge
- Converter slag charging
- Revert charging
- Reducing or oxidizing atmosphere
- Firing rate and effective air/fuel ratio

Other factors that influence the SO_2 evolution include bath agitation, dilution air allowed to enter, separate processing for converter slag, use of bedding systems to minimize charge composition variation, and source of ores.

2.3.3.3 Charge Composition Variation

Some of the smelters operate with foreign ores and some take materials and products from other smelters to give a relatively wide range of feed or charge materials. For example, ASARCO/Tacoma usually processes foreign charge which is high in arsenic and rich in copper and gold. They also produce arsenic trioxide as a product. The ASARCO/El Paso smelter processes not only concentrates, but in addition, copper residues, lead compounds, copper drosses from lead plants, and zinc blends which provides it with a relatively broad range of constituents and feed characteristics. Copper drosses contain relatively small quantities of sulfur. Some smelters, such as Phelps Dodge/Douglas and ASARCO/Hayden, process calcines from roasters. Additional nonconcentrate materials that may be

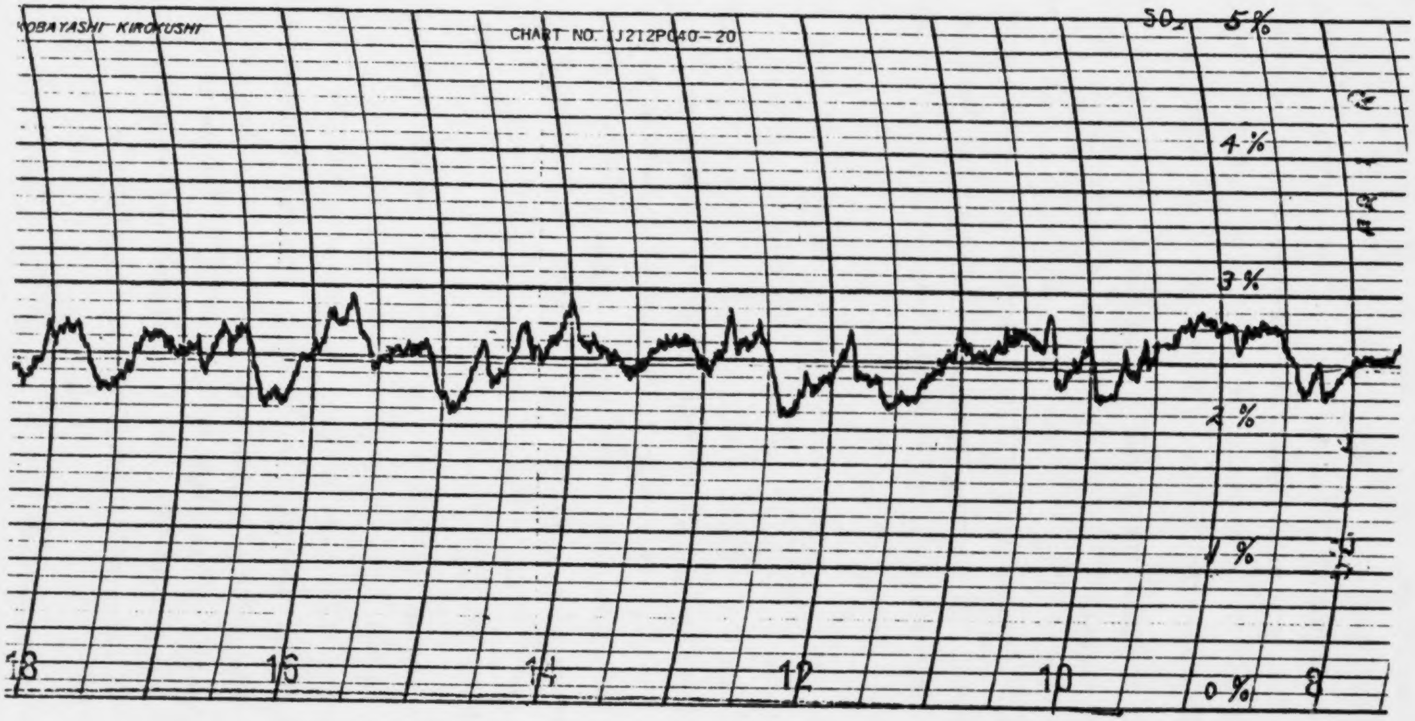


Figure 2-5. Percent SO_2 Emissions Versus Time From Onahama Reverberatory Furnace

added are plant cleanup, Cottrell and/or multiclone dust, scrap brass fines, primary ores of varying nature, "dead" calcine, spill material, raw silica or limestone, acid sludge, silica slurry, revert material, and other materials that are fed to reclaim the copper content or for disposal. In most cases, input material is mixed in bedding systems allowing some control of feed constituents.

The ore or concentrate composition has a very important bearing upon the amount of sulfur which is eliminated in the reverberatory. Calcines usually contain little sulfur in excess of matte requirements. Consequently, calcine-fed furnace gases are lower in SO_2 content. The higher the degree of roast, the less sulfur is present for release in the reverberatory within a reasonable degree of smeltability of the calcine.

Calcine-fed furnaces using a high degree of roast emit the least SO_2 in the exit gases, ranging down to 0.35 percent SO_2. Heat in the calcine reduces energy requirements and consequently reduces nitrogen dilution from combustion air. However, this is balanced by the fact that some sulfur has already been eliminated in the roaster. Wet or green charge furnaces tend to typically emit an average of 1.5 percent SO_2 compared to an average of 0.5 for calcine charge.[6] Matte requirements and specific operating conditions will, of course, vary these results.

Pyritic ore may be defined as a material which tends to lose one atom of sulfur when heated such as FeS_2, CuS, $CuFeS_2$. These materials are unstable at smelting temperatures and, therefore, easily lose their first sulfur atom. An analysis of the feed material to the three smelters producing the SO_2 elimination curves in Figure 2-4 was provided by ASARCO.[7] The percentage of copper and sulfur, with the sulfur-to-copper ratio in the roaster calcine at the three ASARCO smelters is as follows:

	Roaster Calcine (Percent) Cu	S	S/Cu
Tacoma (Curve A)	27.1	25.8	0.952
Hayden (Curve B)	24.0	18.3	0.763
El Paso (Curve C)	24.3	17.9	0.737

From Figure 2-4, Tacoma has the highest SO_2 emissions, followed by considerably lower values for Hayden, then El Paso. Calcine composition, stable sulfides, and pounds of sulfur as stable sulfide per 1,000 pounds of calcine are shown in the following table for the Tacoma smelter:

Calcine Composition (Percent)		Stable Sulfide	Per 1,000 lb Calcine lb S as Stable Sulfide
Cu	27.1	Cu_2S	68.2
Fe	21.5	FeS	123.2
Pb	1.3	PbS	2.0
As	4.7	As_2S	30.1
Sb	0.87	Sb_2S_3	3.4
		Total	226.9

The total sulfur per 1,000 lb of calcine at Tacoma is 258 lb. The pyrite sulfur is equal to 258.0 - 226.9 which is equal to 31.1 lb. Similarly for Hayden, the pyritic sulfur is equal to 18.1 lb and for El Paso 6.0 lb. Thus, more pyritic sulfur is available at Tacoma, and subsequently less at Hayden and El Paso, respectively. The amplitude of the SO_2 elimination curves (Figure 2-4) from their respective reverberatory furnaces follows these numbers. It is, of course, not possible to completely roast all of the above pyritic sulfur, but it can be expected that the SO_2 emission trend would be in the direction of availability.

A so-called "over-roast" or excess removal of sulfur results in smelting difficulties when calcines in this condition are fed to the furnace. When too much sulfur is oxidized, formation of FeS is prevented and iron is forced to go to FeO or Fe_3O_4 magnetite reducing the ability to form matte. Concentrates high in iron pyrites and other iron sulfides have excess sulfur which can result in higher SO_2 in furnace gases in the presence of free oxygen. Additionally, a higher matte grade usually denotes less sulfur in the charge and lower SO_2 emissions. Techniques of charging, frequencies, etc., have little bearing on raising or lowering total SO_2 emitted unless the smelting rate is deliberately varied unproportionally and uneconomically.

2.3.3.4 Method of Charging

Charging methods vary considerably both in terms of handling of the charge and rate at which it is fed into the furnace. There are no smelters in the United States that are top charged (through the center portion of the roof), but some smelters will charge along the wall through the roof, and some will charge through the wall. Those charging calcine through the wall typically use Wagstaff guns, which are essentially chutes that pass the charge into the furnace. At least three per furnace are used, each charging a different area. This charge technique tends to spread the charge over the molten bath more uniformly.

When the charge is dropped along the walls from the top, it tends to build up piles directly underneath the entry points. The Ajo smelter has a belt slinger that actually slings the charge to better distribute it over the molten bath. Calcine charges are usually fed using the Wagstaff or fixed type of gun exclusively. Some smelters will alternate or mix calcine charge at one point and green charge at another point. Mixing calcine and green feed with drag chains was tried at Morenci and then abandoned because of too many problems. Also, Anaconda tried mixing calcine and green charge using a screw conveyor system. This mixing did not prove satisfactory. Alternate feeding of calcine and green charge can result in almost continuous feed. There does not seem to be any direct correlation in sulfur evolution with charge method, only charge frequency.

There also is not necessarily any even or regular charging time. Even though the curves in Figure 2-4 show approximately 20 minute charge times, this does not always hold true and may vary considerably up to even 2 hours for some furnaces and down to 10 minutes for others.

Furnace charging and furnace firing are controlled entirely by the operator. The operator's main criterion for charging and firing is visual observation of the internal portion of the furnace. This includes the flame, the melting charge condition, and the temperature of the refractory which is obtained either by pyrometric means or observation of the brick color. While the operator is continuously pushing the furnace for maximum production, he must be careful not to overcharge. Overcharging can cause the furnace to be "killed" or the temperature to drop. The furnace must be continuously watched as it is being fed, and the charging must be adjusted accordingly. The principle of furnace feeding is to achieve maximum exposure of the charge to heat.

Sulfur evolution primarily depends upon the smelting activity in the furnace. The objective of reverberatory furnace smelting is to use both the heat from the flame above and the heat from the molten bath below. During normal operation of a reverberatory furnace, the stronger SO_2 emissions are generated at the time the charge is introduced and during bubbling or a high degree of turbulence. It is desirable to have intimate contact between slag FeO and silica. This is promoted by the bubbling action. Fine grinding and mixing of the charge before introduction into the furnace will also promote mixing,but the greatest amount or effect occurs with the bubbling within the furnace. Sometimes the bubbling does not occur resulting in reduced reaction rate. When there is a "flat bed" the operator will generally raise the temperature.

With the Wagstaff gun, the calcine charge is floated on the molten bath. There tends to be a more uniform spreading of the charge over the bath, although the rapid input of the material causes SO_2 surges. Even with the floating of the charge, there is still bubbling. The charge may stick in the charge car or gun and require hammering to dislodge. This can change the charge frequency and rate. At other times it may flow into the furnace very rapidly.

Continuous charging which might level off SO_2 fluctuations is not used in many smelters because it tends to cause local overcharging which can reduce the temperature in the furnace below the efficient level. Also, every time there is a charging operation, additional dilution air enters the furnace. The charge material used in the furnace is not always consistent and contains various constituents at different times which also tends to inhibit continuous charging. Some smelters do not have bedding areas and will take the charge as it comes in, also promoting greater variation. For example, at Chino, New Mexico, the concentration copper grade varied from 12 to 25 percent in a period of 3 days.

However, it should be noted that continuous reverberatory furnace charging can and is being used. Detailed discussion of actual operating smelters using continuous charging is presented in Appendix C.

2.3.3.5 Converter Slag Return

Normally, converters are skimmed of slag at hourly intervals. However, variation can range from five ladles in 1 hour to as much as 2 hours with no skimming. Depending upon the composition of the converter slag, there tends to be a large increase in SO_2 evolution when it is introduced into the furnace. Converter slag differs from furnace slag in silica content. This causes increased gas evolution with resulting turbulence, and also in its higher iron oxide and magnetite content. Some of this magnetite is reduced by sulfides present.

The equations relating converter slag reactions are:

$$O_2 + FeS + Fe_3O_4 \longrightarrow 4\ Fe\ O + SO_2$$

Finish Slag

$$Cu_2O + FeS + O_2 \longrightarrow FeO + SO_2 + 2Cu$$

Finish slag may be transferred to the converter and held after the blister has been poured.

An indication of the composition of the reverberatory furnace and converter slag is shown herein.

Slag	Percent FeO	Percent SiO_2
Reverberatory furnace slag	39	38 - 39
Converter slag	50	25 - 26

The principal reason for not returning converter slag to the reverberatory furnace is to eliminate the silica content resulting in less reverberatory furnace slag and less silica. At some smelters, they may have metal value in the slag, such as gold and silver, making it more worthwhile to process the converter slag rather than return it to the converters.

It is, of course, possible to eliminate the SO_2 peaks due to converter slag return by processing the converter slag in a concentration system (refer to Appendix D). Processing the converter slag separately also tends to reduce the amount of magnetite that enters the reverberatory. It is also more expensive. Kennecott/ Hayden and several other smelters slow cool their converter slag in pits and send it back to the concentrator for retreatment.

2.3.3.6 Charge Bank Sloughing

Emission variations occur when, for example, with side wall charging,a section of the bank will slough off and cause a rapid reaction because of the greater surface exposed to the molten bath. This will be accompanied by an increase in SO_2 production.

There is a minimum of charge-sloughing in calcine-fed furnaces unless large piles of calcine are accumulated due to force-feeding in specific areas. With green feed furnaces, there is always the likelihood of sloughing unless charge banks are specifically maintained for maximum smelting. Automatic or careless charging can result in overcharging some areas and increases the likelihood of sloughing. A properly operated furnace has practically no sloughing.

Another factor causing sloughing is undercutting of the charge banks by the liquid bath,thereby also increasing the reaction area. This is especially prevalent when matte is tapped from the smelting zone (under charge piles), instead of near the outlet end of the furnace.

The magnitude of gas evolution during any sloughing is a function of the amount of charge that reacts with the bath and any moisture that may be present which is converted to steam. If the concentrate is not partially dried and the charge contains excess moisture, there is naturally more steam evolved. If the sloughing is violent enough to allow contact of heavy moisture-laden material with the matte in the bath, an explosion inevitably results from rapid evolution of steam and hydrogen sulfide.

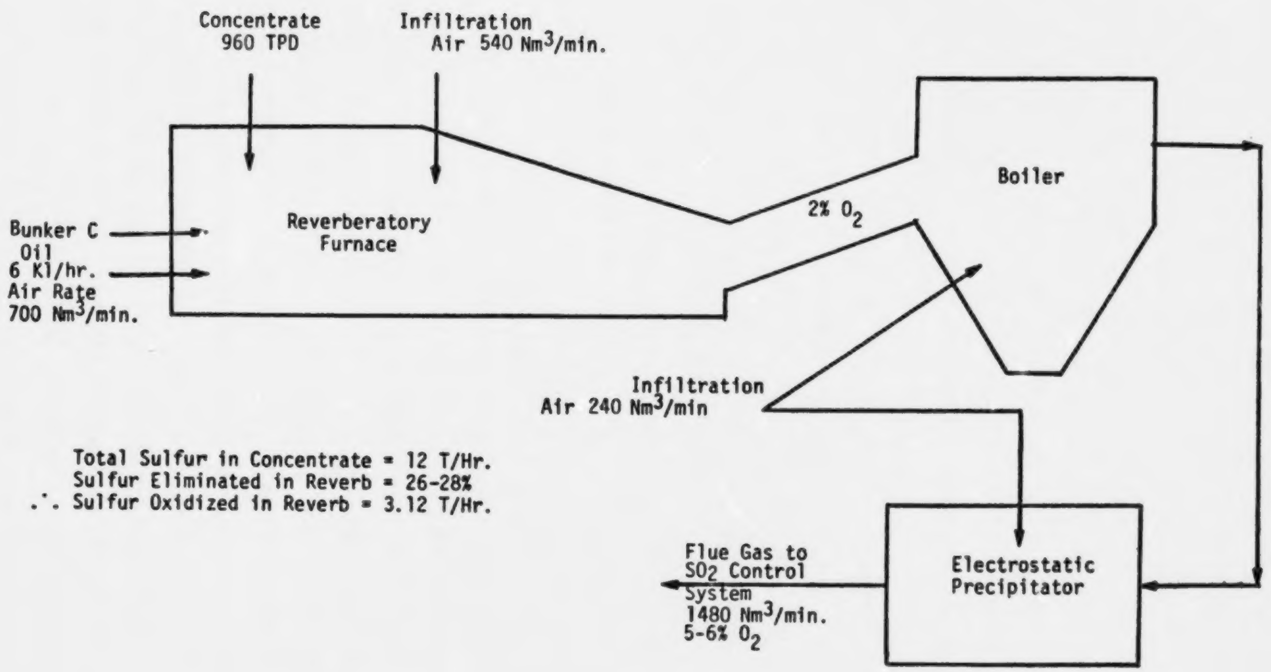
2.3.3.7 Furnace Firing Conditions

The furnace is operated under negative draft. The amount of infiltration air that enters the furnace is primarily dependent upon the effective open area resulting from cracks, gaps, and ports as well as the operating pressure. In addition, primary and secondary air may be introduced at the burner along with the fuel. The moisture in the charge and the combustion and smelting reactions all contribute gases making up the total flue gas.

The ratio of fuel to the total air entering the furance will be the major factor in determining whether the gases are oxidizing or reducing. If a reducing atmosphere can be achieved in the furnace, an increase in SO_2 concentration can be expected. On the other hand, the lower the air-to-fuel ratio, the lower the heat release per unit weight of fuel.

The reason a higher SO_2 concentration occurs under more fuel-rich conditions is that the amount of air entering is reduced by the dilution effect of the additional nitrogen. This is illustrated by the operation at the Onahama smelter in Japan where SO_2 concentration out of the reverberatory furnace averages 2.6 percent without oxygen enrichment.[8] Figure 2-6 shows a gas material balance for the Onahama reverberatory furnace. Calculations indicating interactions within the furnace are presented in Appendix E and discussed in Section 2.4. The total volume of air required for stoichiometric combustion of the fuel is 1,948 Nm^3/min (33,474 scfm). The total volume of air required for bath sulfur oxidation is 183 Nm^3/min (6,468 scfm). Thus, total volume of air required for combustion of fuel and bath sulfur oxidation is 1,131 Nm^3/min. The 1,240 Nm^3/min (43,790 scfm) air used in the furnace entering from burner air and infiltration indicates that the furnace is being operated with approximately 10 percent excess air which could be used up by some oxidation of iron sulfide. In any case, this would seem to indicate that the furnaces are being operated very close to or even slightly on the fuel rich side of the stoichiometric air to fuel ratio. Also, the above analysis shows that at least 25 percent of the air required to burn the fuel is obtained from the infiltration component. The fact that average SO_2 concentration in Japanese green charge reverberatory furnaces is in the 2 to 3 percent range compared to 1.5 percent typically for U.S. smelters may partially be explained by operation in the more fuel rich range. Extensive sealing of all openings in the furnace and downstream gas handling system as well as relatively close control of furnace pressure minimizes infiltration air, also tending to increase SO_2 concentration.

Preheating of burner air will also tend to increase SO_2 concentration by reducing the amount of fuel that is required in the furnace to maintain smelting temperatures. Combustion gases and the diluting nitrogen are of course reduced. It is estimated that


Concentrate
960 TPD
Infiltration
Air 540 Nm3/min.
Bunker C
Oil
6 Kl/hr.
Air Rate
700 Nm3/min.
Reverberatory
Furnace
2% O2
Boiler
Infiltration
Air 240 Nm3/min
Flue Gas to
SO2 Control
System
1480 Nm3/min.
5-6% O2
Electrostatic
Precipitator

Total Sulfur in Concentrate = 12 T/Hr.
Sulfur Eliminated in Reverb = 26-28%
∴ Sulfur Oxidized in Reverb = 3.12 T/Hr.

Figure 2-6. Schematic of Onahama Reverberatory Furnace Gas System

preheating the reverberatory furnace secondary burner air at the Onahama smelter to 400°C (751°F) increases SO_2 strength by 0.1 to 0.2 percent. The use of separate oxygen fuel burners increases the SO_2 by 0.3 percent for each burner used (refer to Section 3.9.).

2.3.3.8 Reduced Operation Effects

To maintain maximum efficiency and economy, it is desirable to prevent any reduction or cessation of operations. Various plants use different techniques during operational varations, but none are as economical as undisturbed operation.

In spite of undesirable effects, it is occasionally necessary to reduce or suspend operations. The heat loss through the brick arch and furnace walls is somewhat constant but does vary slightly as a function of the internal heat. Unless a furnace shutdown is indicated, the internal heat must be maintained sufficiently to keep the bath molten whether the furnace is smelting or not. The exit gases will be reduced in volume but only slightly reduced in temperature. Sulfur dioxide content will drop proportionally to any remaining smelting or roasting action within the furnace.

The alternative for furnace shutdown is to smelt out all the charge, completely drain the liquid bath, and then seal all furnace openings and close all dampers. This allows the completely sealed furnace to start cooling down. It will then take from 2 weeks to a month for the furnace to cool down completely with bottoms retaining high temperatures 200°C (400°F) for several months unless air and water cooling is used. Upon startup, it will then be necessary to preheat for at least 2 weeks at 93°C (200°F) rise per day average to get the unit up to smelting temperature. Furnace gases will start containing SO_2 as soon as any new charge is again smelted.

2.3.3.9 Fuel Supplied Sulfur

Sulfur in oil or coal fuels can contribute to the SO_2 released in the reverberatory furnace. There is usually no significant sulfur from this source if gas is used as the furnace fuel.

For example, at the Onahama smelter, Bunker C oil is used with a 2.5 percent sulfur content. This produces approximately 3.5 percent of the total SO_2 volume generated in the furnace. Refer to Appendix E for calculations.

It can be expected that, in the near future, more smelters will be using oil and eventually pulverized coal in the reverberatory furnaces because of the energy situation in the United States.

2.3.3.10 Sulfur Dioxide Stratification

It is known that vertical stratification of SO_2 concentration generally exists in the reverberatory furnace. At Onahama, the maximum concentration of SO_2 appears approximately 1 m above the bath and decreases form this point to a negligible amount at the roof.

Table 2-1 and Figure 2-7 summarize sample data taken by Kennecott at the Magna, Utah smelter[9] reverberatory furnace and also indicate high SO_2 concentration at the bath level with reduction toward the roof.

As the gases are passed through the furnace uptake, waste heat boiler and precipitator, they become mixed and this stratification effect disappears (Table 2-1). There have been no attempts to collect the richer SO_2 streams for processing.

Table 2-1. AVERAGE DRY GAS COMPOSITION (PERCENT BY VOLUME) AND FURNACE DRAFT AT VARIOUS SAMPLING STATIONS NO. 1 REVERBERATORY FURNACE[9]

Sampling Station	1		2			4			5			6		7	
Sampling Point	1A	1B	2A	2B	2C	4A	4B	4C	5A	5B	5C	6A	6B	7A	7B
% SO_2	0.8	0.9	0.7	0.9	0.9	0.8	0.8	1.0	0.7	1.1	1.1	1.1	1.3	1.0	1.1
% CO_2	9.2	9.3	9.1	9.1	9.3	9.6	9.5	9.7	9.3	9.8	9.4	9.9	9.3	9.3	9.8
% O_2	3.3	1.7	2.6	1.7	1.7	1.9	1.3	0.9	2.6	1.4	1.1	2.2	2.3	2.5	2.0
% CO	0.3	0.7	0.4	0.6	0.5	0.0	0.1	0.2	0.1	0.0	0.3	0.0	0.0	0.0	0.0
Draft (in. H_2O)	0.14	0.14	0.05	0.10	0.12	0.09	0.10	0.11	0.10	0.09	0.08	0.01	0.03	0.02	0.03

(1) Reported as % dry gas at saturation point of 80°F.

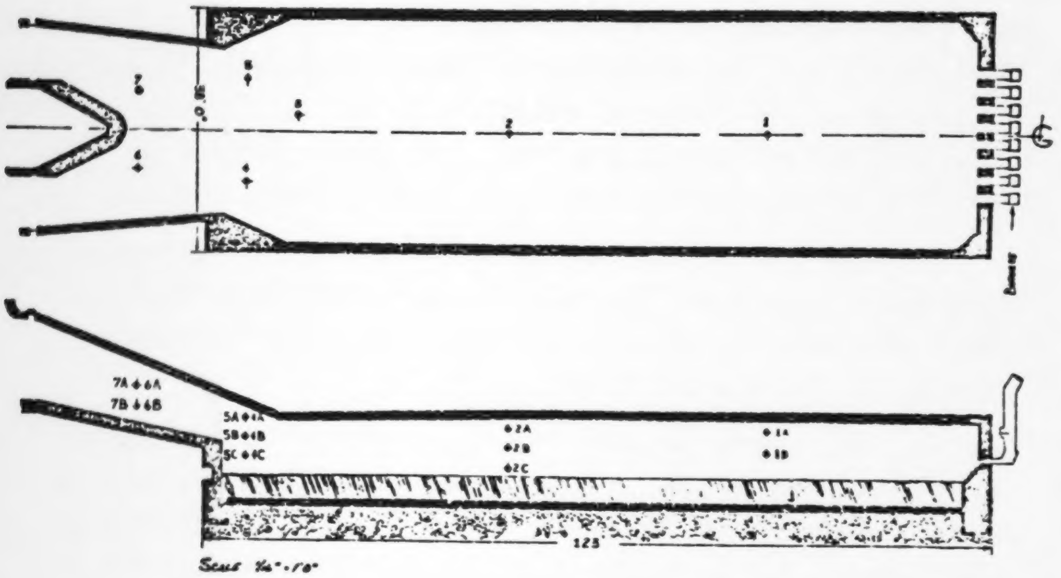


Figure 2-7. Sampling Stations and Points
No. 1 Reverberatory Furnace

2.3.4 COMPARISON OF U.S. AND JAPANESE REVERBERATORY FURNACE PRACTICE

A description of the Onahama and Naoshima smelter reverberatory furnaces and general operating practice in Japan is presented in Appendices F and G, respectively. In general, there is no appreciable difference in construction between the green charge reverberatories at Onahama and the calcine reverberatory at Naoshima when compared to U.S. designs. Actually, they were designed by a U.S. consultant.

Figure 2-6 is a schematic of an Onahama reverberatory furnace gas system with typical values of material flow. A material balance was made in an attempt to determine the differences between U.S. and Japanese furnace practice that results in higher SO_2 off-gas concentrations in Japan. Appendix E summarizes the results.

These calculations indicate (and it was later confirmed by Mitsubishi Metals Co.) that the Onahama furnaces are operating with below theoretical air in the burner end of the furnace and total air supplied is only 10 percent over theoretical. This could explain a difference in SO_2 concentration. It can also result in lower fuel efficiency.

Although the reverberatory furnaces are almost conventional in design and operation, the following summarizes those factors that appear to contribute to higher SO_2 in the Onahama reverberatory gas as compared to U.S. experience:

1. The furnaces are very tightly constructed and kept sealed so as to minimize air infiltration. There are no external openings to the furnaces except those necessary for burners, slag receiving, and charging. All unnecessary openings developing are calked with mineral wool and cements applied by hand trowel. Bridgewall burner clearances are minimal. Slag spout openings are tightly closed by doors when launders are withdrawn and all spout cleaning is done external to the furnace. There are no side openings in the furnaces, and charge ports are kept sealed whenever charge is not being admitted. Only one of three ports on each side of the furnace are usually open at one time. There appears to be no need to bar down for port cleaning. The charge is dried to less than 8 percent moisture before being charged so it is free flowing through ports and on furnace banks, resulting in less moisture-caused volume increase in furnace gases.

2. Combustion air is kept below theoretical and with infiltration air is only 10 percent over theoretical for sulfur and fuel oxidation.

3. As most of the concentrates are shipped to Japan from foreign sources, their producers, because shipping costs are based on weight and not grade, endeavor to ship concentrates of highest possible grade. As sulfur is combined with copper in the common minerals, the concentrates are generally high in sulfur content (at least 28 percent). Also at Onahama, other minerals that may be smelted in reverberatories in the U.S. such as secondaries, cement copper, scrap brass fines, dusts (pelletized), etc., are all smelted in the converters.

4. Natural gas fuels used in most U.S. smelters have been desulfurized so there is no sulfur input from the fuel source. The dryer furnace feed in Onahama tends to slightly enrich furnace gas SO_2 by decreasing volume resulting from the reduction in furnace fuel requirements.

5. Preheating of the secondary air has contributed to more rapid smelting and consequent release of combined sulfur. This is estimated to increase SO_2 strength by 0.1 to 0.2 percentage points. A higher degree of air preheat would increase the percent SO_2 further. Additionally, the use of oxy-fuel burners accelerates the smelting rate. It is claimed that each burner results in an overall SO_2 increase of 0.3 percent in exit gases.

6. Contributing to the increased smelting rate is the large sizing of the cross sectional areas of the furnaces in the smelting zone. Nearly all other plants do not have this feature although it was originally conceived in the old Arizona United Verde in the 1920's. The furnace outlet flues are also larger in cross section which results in lower pressure drop. The lower pressure drop allows operation at negative pressures closer to atmospheric which minimizes leakage of dilution air.

7. Combustion and feeding are instrument-controlled so as to produce a steady level of operation,and furnace interiors can be observed by closed-circuit TV at all times. Needed minor adjustments to furnace operations can be made almost instantly, before adverse conditions can do any harm or affect the steady flow of maximum SO_2. Assays of slag, silica, mixed ore, and matte can be obtained within an hour to further indicate and facilitate needed adjustments. Daily composites are normally analyzed each 24 hours by a Phillips X-ray Spectro Meter connected to a computer readout.

No other factors were found that influenced the higher Japanese SO_2 content than is considered normal for U.S. furnaces. The SO_2 is sampled after furnace gases pass through the waste heat boilers and electrostatic precipitators and are entering the treatment plants so actual furnace gases would contain a fraction higher. This effect is minimized by the straight-through two drum type boilers with air tight ash pits containing no baffles or diverters, making them practically air tight. The precipitators are of welded construction and are well insulated, appearing to be airtight. All units in the sequence are spaced very closely together, thus there are no long flues to leak, contrary to most older smelters.

The maintenance and operation of the calcine charged Naoshima reverberatory furnace is similar to that at Onahama. Greater use of television observation of the bath allows very close control of smelting conditions. As the charge is fed from each Wagstaff gun, the activity in the furnace is continuously visually monitored. It is possible to tell, very closely, when the previous charge in a given area has been dissolved in the bath (bubbling action) and when the next charge in this area can be fed. Operation of each gun is controlled by a switch in easy reach of the operator.

Certainly our green-feed smelters could follow practices and construction similar to those employed by the Japanese with equal or better results if efforts were to be directed towards this objective. There has been no concentrated effort to raise reverberatory gas strengths in U.S. smelters as even 2.5 percent would not allow economic recovery by present means. Upon recent questioning of responsible supervisors at two Arizona smelters, it was stated that little attention was paid to reverberatory gas strength in their plants, but they felt sure it varies between 1 and 3 percent under different operating conditions. In other instances, where only periodic sampling of reverberatory furnace gases was done, the SO_2 content was usually found to be in the 1 to 2 percent range so that treatment was considered completely uneconomical. As will be indicated in the following discussions, the higher the SO_2 concentration, the smaller the size generally required for any subsequent control system.

2.4 CONVERTING

Molten matte is processed in two or more Peirce-Smith Converters. These converters are horizontal, cylindrical basic-lined vessels, typically 13 feet in diameter and 30 to 32 feet long. Flux containing preferably 70 to 80 percent silica is added, and air is blown into the matte through submerged tuyeres to oxidize the iron and sulfur content of the matte. The iron oxide formed combines with the silica flux to produce an iron silica slag that is skimmed off. Molten temperatures of 2,100°to 2,200°F are maintained as a result of the oxygen's reaction with iron and sulfur which is exothermic. Regular additions of cold copper bearing materials are required to limit converting temperatures. Further details are given in Appendix H.

All but 1 or 2 percent of the iron and a considerable portion of the sulfur is oxidized prior to skimming off the iron silicate slag, leaving a "white metal," about 70 percent copper and 24 percent sulfur. This is known as the slag blow which produces average offgas SO_2 concentrations of 10 percent. When collected by the primary converter hood, this value will be diluted to 5 percent average. Further blowing converts most of the remaining sulfur to SO_2 leaving a final blister copper usually containing about 98.5 to 99.3 percent copper, 0.3 percent sulfur, some dissolved oxygen, and other impurities. This is called the copper blow and can produce SO_2 concentrations in collected gases in the converter hood in the range of 6 to 8 percent. The blister may be further refined in a reducing atmosphere and either cast into cakes for shipment or into anodes for further electrolytic refining.

It should be noted that the initial impurity mix in the converter will determine to a great extent the blowing time for the converter operation. If lead is an impurity, for example, a long converter blowing time is required. This is accomplished by producing a low grade (high sulfur) matte from the reverberatory furnace. This indirectly can effect the weak SO_2 stream generation in the furnace as well as the operation of both the roasters and the furnace.

2.5 CONVENTIONAL SULFURIC ACID PLANT PRACTICE

Most domestic experience in SO_2 control for copper smelters has been with capture by conversion to sulfuric acid. This is the most readily available approach for SO_2 control and has been used on SO_2 offgases from roasters and converters for a number of years. Lean SO_2 offgases (0.5 to 1.5 percent) from reverberatory furnaces, however, have rarely been captured and usually are emitted directly to the atmosphere because of the inability of a conventional acid plant to economically process this low concentration range.

2.5.1 SULFURIC ACID PLANT TECHNOLOGY

2.5.1.1 System

The process for the manufacture of sulfuric acid from copper smelter offgases consists of three principal steps; namely:

- Purification of SO_2 gas from the smelter
- Conversion of SO_2 gas to sulfur trioxide (SO_3) gas
- Absorption of SO_3 in H_2SO_4

A schematic of a single or double contact (see section 2.5.1.3) acid plant is shown in Figure 2-8.

2.5.1.2 Conditioning of SO_2 Gas

Smelter gas can normally contain combinations of SO_2, metallic fume, dust, SO_3, and gaseous impurities. The SO_2 gas stream entering the acid plant must be clean and dry to minimize operational problems.

The gas is usually cooled in passing through a waste heat boiler or other heat exchanger sufficiently to enter a precipitator for major particulate removal. The gases then pass to a spray chamber or cooling tower where water removes many of the remaining impurities and further cools the gas. Scrubber equipment has also been used for this purpose. The gas must be cooled to reduce its moisture content. Final cooled temperature is determined by the SO_2 concentration, product acid strength desired, cooling water temperature, and the elevation of the plant above sea level.

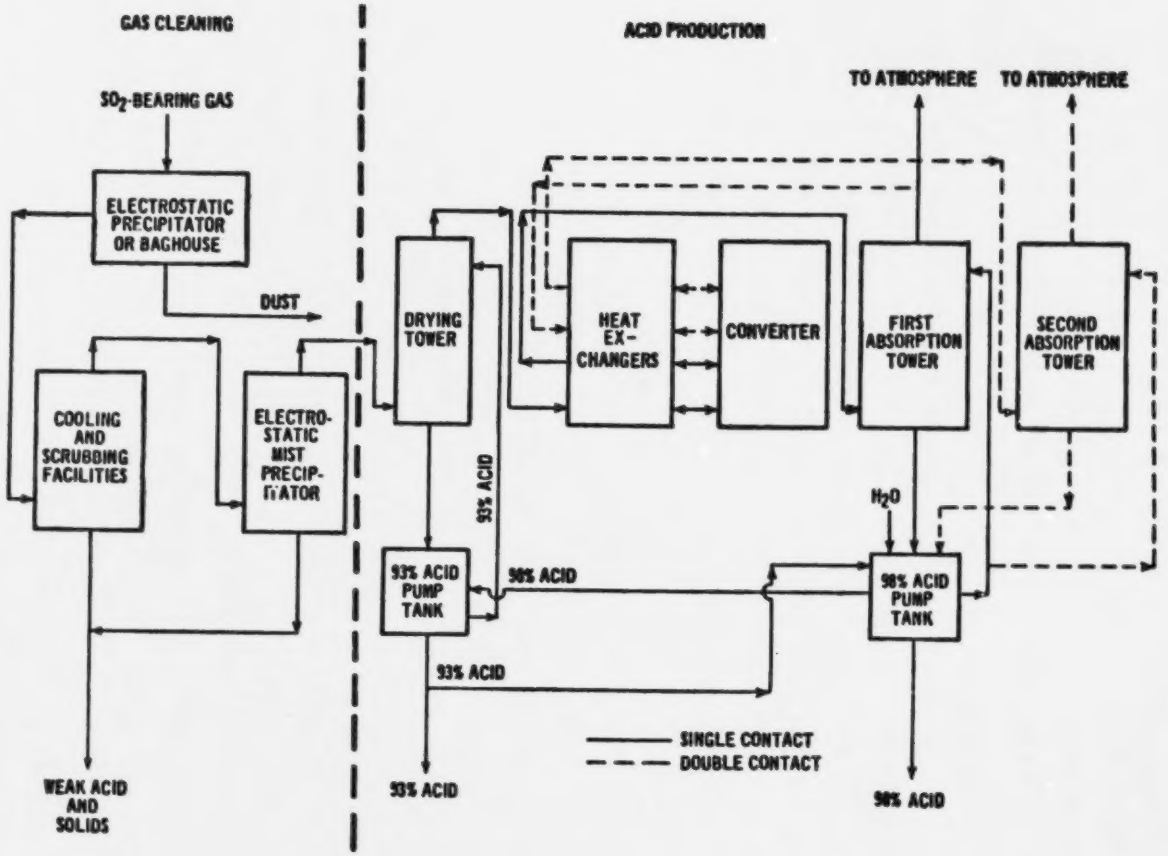

GAS CLEANING
ACID PRODUCTION
SO_2-BEARING GAS
ELECTROSTATIC PRECIPITATOR OR BAGHOUSE
DUST
COOLING AND SCRUBBING FACILITIES
ELECTRO-STATIC MIST PRECIP-ITATOR
WEAK ACID AND SOLIDS
DRYING TOWER
93% ACID
93% ACID PUMP TANK
98% ACID
93% ACID
93% ACID
HEAT EX-CHANGERS
CONVERTER
FIRST ABSORPTION TOWER
SECOND ABSORPTION TOWER
TO ATMOSPHERE
TO ATMOSPHERE
H_2O
98% ACID PUMP TANK
98% ACID
SINGLE CONTACT
DOUBLE CONTACT

Figure 2-8. Single and Double Contact Sulfuric Acid Plant Schematic

The water discharged from the spray chamber or cooling tower will contain the impurities removed from the gas and will also be saturated with SO_2 from the gas. To recover sulfur values and reduce effluent nuisance, this water may be passed through a stripping column where a stream of air removes most of the SO_2 from the water. The SO_2 gas so recovered is fed back to the tower. The water from the stripping column then may be either neutralized or discharged.

The gas leaving the cooling section is passed through a mist precipitator in which most of the remaining particles of acid mist, metallic fume, and dust are removed by electrostatic precipitation. Sulfuric acid mist generally contains particles less than 5 microns and is very difficult to remove from the gas stream except with an electrostatic precipitator. If this mist is allowed to enter the contact section of the acid plants, it will cause corrosion problems in carbon steel ducts, heat exchangers, and the main blower.

The usual mist precipitator is a tube type with verticallead tubes 6 to 10 inches in diameter. High voltage discharge electrodes are suspended in the center and run the entire length of the tubes. The mist particles are attracted to the tube walls, flow downward,and are collected in the lower header in the form of 5 to 10 percent H_2SO_4. Two mist precipitators installed in series can provide 99 percent removal efficiency. There are two two series of precipitator banks because the entrained acid in the gas stream tends to produce arcing and requires a reduced input voltage lowering the efficiency of the unit. With two units in series, the voltage is reduced only to the first unit so the overall efficiency is affected only slightly. In some cases, only one precipitator is used to minimize capital expenditures with resulting lower efficiency.

The gas passes from the mist precipitator to the drying tower where it moves up through a bed countercurrent to the flow of 93 percent acid. The acid absorbs the moisture remaining with the gas which is to a maximum water vapor content of 5 mg/scf. The heat generated by the absorption of water in the circulating acid is removed in heat exchangers cooled with water, reducing acid temperature to approximately 105°F.

For high SO_2 to SO_3 conversion efficiency, the converter entrance gas should contain at least 1.3 volumes of oxygen for every volume of SO_2. This ratio maximizes the gas strength out of the converter and determines the required volume of gas handled per ton of sulfuric acid produced. Introducing additional air to supply oxygen may be necessary in cases where this ratio is not maintained.

The main gas blower usually follows the drying tower to provide sufficient suction to pull the air required through the purification system and sufficient pressure to blow the gas through the converter heat exchanger system and the absorption tower. Blower static pressure capability is typically 150 in. w.c.

The gas leaves the blower at about 130°F and flows through a series of heat exchangers in which its temperature is raised to 820°F, the required temperature for entering the first catalyst layer in the converter.

The dry gas leaving the blower passes through the shell side of three (usually) shell and tube heat exchangers in series in which its temperature is raised to 820°F. In the cold heat exchanger, the SO_2 gas is heated to approximately 480°F as it flows countercurrent to the SO_3 gas leaving the converter. In the intermediate exchanger, the SO_2 gas is further heated to about 555°F by cooling the gas leaving the second bed of the converter. Further heating of the SO_2 gas to 820°F is accomplished in the hot, or converter, heat exchanger by cooling the partially converted gas leaving the first catalyst bed from about 1,075F to 820°F. Suitable bypasses are provided around these exchangers to permit maintaining optimum temperatures to the converter.

2.5.1.3 Conversion of SO_2 to SO_3

The conversion of SO_2 to SO_3 takes place in the converter. The converter contains several layers of a vanadium pentoxide catalyst, the purpose of which is to accelerate the reaction between SO_2 and oxygen to form SO_3. The converter is normally of the three-stage four-bed type, designed to provide maximum conversion efficiency.

The heat of reaction generated in the first stage of conversion where 70 to 75 percent of the SO_2 reacts with O_2 in the gas stream is removed from the gas in the external converter heat exchanger. The temperature rise may be 250 F° to 300 F°. The rise in temperature reduces the conversion equilibrium.

The partially converted gas, cooled to 830°F in the converter heat exchanger, is returned to the second stage. The heat of reaction in the second catalyst bed is also removed in an external intermediate exchanger. Heat from the third and fourth beds is removed in the external cold heat exchanger.

An indirect air cooler can be used to reduce the SO_3 containing gas temperature to 300°F to 350°F before going to the 98 percent sulfuric acid recirculating over the absorption tower. The heat rise in the acid resulting from (1) the transfer of 93 percent acid, (2) heat of absorption of SO_3 and (3) from the sensible heat in the incoming gas, is removed from the acid as it flows by gravity through the 98 percent acid cooling heat exchangers to the pump tank. The exchangers are designed to reduce the acid temperature to 150°F. A vertical submerged pump recirculates the 98 percent acid over the absorption tower where the SO_3 is absorbed to form produce 98 to 99 percent acid which is then delivered to the acid storage coolers or to the 93 percent acid system for dilution.

For heating the converter system, valved ductwork is provided from the blower discharge to a heat source, either as a separate gas-fired heater or from some other source in the plant.

The double contact acid plant is the same as a single contact except that the partially stripped gases at a higher SO_2 to SO_3 ratio are again passed through a portion of the converter and a second absorption tower. With this approach, a 500 ppm SO_2 acid plant emission can be guaranteed, as compared to 2,000 ppm for a single and double contact sulfuric acid plant schematic.

A clear discussion on some of the relative merits between single and double contact systems for metallurgical plants is presented below from Reference 10.

> "High sulfur dioxide concentrations are advantageous because they produce more acid for a given size plant. However, oxygen concentrations decrease as sulfur dioxide concentrations increase, and the oxygen concentration has a significant effect on catalyst performance and yield. For this reason, optimum sulfur dioxide concentration in a conventional metallurgical type contact plant is approximately 7.0 to 7.5 percent by volume. In the double contact or "interpass absorption" type plants first developed by Bayer in Germany, the optimum concentration is approximately 9.0 percent SO_2.
>
> However, equipment must be added to handle this stronger gas.
>
> As sulfur dioxide concentration decreases, smaller fractions of the reaction heat are available to preheat incoming cold gases. At approximately 3.5 to 4.0 percent SO2, the acid plant is thermally balanced and any lower concentrations require the addition of external heat. The preheater provided for plant startup can be used for this purpose but its continuous operation adds extra maintenance and fuel costs to the cost of acid production. It should also be noted that heat exchanger sizes increase rapidly as sulfur dioxide concentration decreases. With the double contact process, thermal balance occurs at approximately 6.0 to 7.0 percent SO2 with 7.5 percent preferred as a practical lower limit.
>
> The conventional acid plant is considered to be a single contact (single absorption or single catalysis) process. This usually results in three passes of the gas through the converter with interstage cooling. Vendors will not guarantee any less output from the sulfuric acid plant than 2,000 ppm with this system. For vendors to guarantee operation with SO_2 emissions at 500 ppm it is necessary to go to the so-called double contact (double absorption or double catalysis) process where the main stream is brought out of the converter loop and a major portion of the SO_3 is removed from the gas in an intermediate absorption tower after a two or three pass conversion. The balance of the gas is returned to the converter for a final one or two stages of conversion taking advantage of the kinetics to drive the SO_2 to SO_3 with a low initial concentration of SO_3."

The difference between single contact and double contact plants as far as additional equipment for the latter is concerned includes the absorption tower, additional heat exchangers and coolers, as well as pumps, valves, and dampers. While there is more equipment in a double contact plant, considering the kind of equipment and the possiblity of designing redundancy into the system, properly designed plants whether single or double contact should not exhibit a difference in reliability. A properly designed plant is one that is specifically designed for potential problems and one that has backup equipment such as spare pumps, valves, and dampers, etc. In many cases, with proper circuitry, it is possible to arrange a system that will allow bypassing of specific pieces of equipment. This will prevent plant shutdown while the equipment is replaced or repaired. Designing for recognized problems will add to the initial capital cost of the plant, but will be economical in terms of total maintenance cost over the life of the plant. The reliability of an absorption tower, where there are no moving parts, is extremely high. Reliability of rotating or moving machinery tends to be lower, therefore, design factors can be incorporated to compensate. Thus, although there is additional equipment, there should not be a major difference in the on-time between single and double contact. This is particularly evident if the system is designed to allow redundancy and minimum maintenance.

2.5.1.4 Acid Plant Design Considerations

High levels of solid or gaseous contaminants in smelter offgases can present difficulties in the production of sulfuric acid if not effectively removed prior to processing. The major problems caused by residual quantities include plugging of the catalyst beds with deactivation of the catalyst and possible contamination of the product acid. These problems, however, are generally rectified by (1) the use of more efficient dust or mist collectors, and (2) the scrubbing of the gases with liquids which absorb the contaminants. Likewise, annual repair of the equipment and catalyst screening will ensure proper acid plant performance.

In some cases, contaminants may affect the final acid product by passing through the gas cleaning equipment and the catalyst.

One such condition is the so-called "black acid" -- resulting from various volatile organics bypassing both the gas cleaning equipment and the catalyst and being captured in the acid product. This situation is more common with multihearth roasters where various organics entrained with the concentrates are merely vaporized or only partially decomposed. However, within fluid-bed roasters, these organic flotation agents are completely decomposed. Thus, sulfuric acid produced from these offgases is free of organic contamination.[11] Nevertheless, there are outlets for sulfuric acid which are not sensitive to color, such as the production of fertilizers or alkylation processes at refineries.

One additional consideration for an economic functioning acid plant is the oxygen content of the gases to be processed. If the oxygen content of these gases is not sufficient to convert SO_2 to SO_3, then additional oxygen must be added to provide the proper ratio of oxygen to sulfur dioxide. For single contact sulfuric acid plants, this oxygen to sulfur dioxide ratio should be at least from 1.25 to 1.3. Double contact acid plants require ratios of at least 1.18 to 1.22.[12]

SECTION 3

PROCESSING TECHNIQUE MODIFICATIONS

3.1 GENERAL

There are processing techniques and variations that have been used at various smelters affecting reverberatory furnace SO_2 generation. Some of these techniques are on an experimental basis and some are under normal production conditions. In general, these techniques have not been primarily applied for SO_2 control but rather to improve operating conditions (e.g., reduce magnetite formation) or to increase production. However, the effects have been to change the SO_2 concentration in the reverberatory furnace offgases.

After reviewing the possible approaches to SO_2 control, it is evident that an increase in concentration of SO_2 in the offgas is desirable. This tends to reduce the cost of processing equipment such as FGD or concentration systems as well as sulfuric acid plants. It is also desirable, in all cases, to minimize the gas volume leaving the furnace by reducing the infiltration of air through elimination or reduction of leakage points in the gas handling system. This minimizes initial and operating costs of the gas handling equipment. (There are, however, several exceptions, as discussed in Section 3.6.)

Sulfur dioxide control from the reverberatory furnace can be facilitated by the following processing techniques related to operation of the smelter.

- Pressure (draft) control
- Elimination of converter slag return

- Sealing all leakage points to reduce infiltration air
- Preheat air supplied to the furnace
- Preliminary processing of charge using a fluid-bed roaster
- Operation at lower air-to-fuel ratio
- Instrumental control of reverberatory smelting to stabilize operations
- Oxygen enrichment
- Predrying wet charge
- Continuous furnace charging
- Elimination of reverberatory furnace
- Converter scheduling and hooding
- Blending

These techniques are discussed in subsequent subsections.

It should be emphasized (see Section 5.0) that each technique will be applicable only under certain conditions depending upon the site specific operations and economic factors and these conditions can change with time for any given smelter. Furthermore, these techniques have been and currently are being used within the industry, not necessarily on a general basis or specific to aid in weak SO_2 stream control.

3.2 ELIMINATION OF CONVERTER SLAG RETURN

Converter slag is returned to the reverberatory furnace through the converter slag return launder. This may be a simple channel with an opening in the furnace wall. It can also be a mechanically operated chute that is inserted through an opening normally covered by a mechanically activated door.

Fifty or more ladles of converter slag can be returned in a 24-hour period. This depends upon the number of converters and the operating level of the smelter.

Each time the slag is returned, a large amount of air enters the furnace for a minimum of 5 minutes and tends to reduce SO_2 concentrations. Conversely, the agitation in the bath and increased chemical reactions with the slag constituents tend to increase SO_2 emissions. However, the overall effect is to reduce average SO_2 concentrations. Consideration should be given to cutting back on primary burner air or using compensating pressure control system operation to minimize fluctuations.

At the very least, converter slag return increases the volume of reverberatory furnace offgas. In some cases, the slag return opening may not be closed at any time, further compounding the SO_2 control problem. Of course, the mechanically activated door and chute technique will minimize infiltration as long as maintenance problems do not become overwhelming.

More and more smelters are weighing the economic advantages and disadvantages of returning converter slag to the reverberatories. For those smelters plagued by magnetite and its buildup in furnace bottoms or hearths and copper entrainment in furnace slag, the elimination of the magnetite source in the converter slag has resulted in much improved furnace conditions. Generally some smelters using green feed have been able to practice magnetite control in the furnaces and still prefer the return of hot converter slag to the furnaces. The advantages and disadvantages of converter slag return are listed in Appendix I.

It has been firmly established in many experiments, e.g., Appendix D and Reference 14, and by the many plants treating converter slag by flotation techniques, that the slag must first be slow-cooled. The formation of crypto-crystalline or ultra microstructures that are too small to separate mechanically for subsequent flotation processes is thus avoided. The larger particles, which are essentially "grown" on a nucleus, are much more amenable to the flotation process for copper recovery when slow-cooling is practiced. The proper length of time required for slow-cooling is somewhat conjectural, but 24 hours is minimal. However, a proper mean is probably from 1 to 2 or more days.

A content of 3 to 6 percent copper in the original converter slag usually results in a copper flotation tailings loss of 0.3 to 0.4 percent. The copper reclaimed from the slag is in the form of a concentrate, which usually contains 20 percent or more copper. This is then returned to the furnace charge or pelletized and smelted in the converter vessels. The copper lost in the tailings is generally in the form of compounds in oxide or silicate form. If economical, they could, however, be leached from the tailings by sulfuric acid treatment followed by precipitation with iron scrap.

Slag magnetite content as high as 53 percent has been determined although this figure is normally 17 to 35 percent in various smelters. After flotation treatment, the concentrate usually contains nearly 5 percent magnetite. The balance is passed into the waste tailings and eliminated.

Within economic limits, grinding of slags is desirable for proper separation of mineral sulfides. Grinding to at least 85 percent minus 200 mesh is not uncommon.

Most flotation treatment of converter slags is done within a circuit separate from ore treatment because of different reagents and techniques required, although a few plants simply add the slag to the incoming ore at the concentrator crusher without noticable detrimental effects. Much of the difference is due to the various flotation circuits used for treating ores in a specific location.

3.3 SEALING LEAKAGE POINTS

To decrease the volume of exit gases and raise the SO_2 concentration, it is always desirable to seal reverberatory furnaces as much as is needed to eliminate air infiltration over the quantities required for good furnace operation. Because there has not been any great need for extensive sealing in reverberatory furnaces in the U.S., in many cases, a large effective open area is available for air to enter. There are some furnaces that have the walls built with gaps between the bricks so great that the fire can be seen through the wall. To eliminate excess air infiltration and thereby decrease volume of exit gases and raise their temperature, it is always desirable to seal reverberatories as much as possible. While infiltration air into the furnace itself can be used for refractory cooling and oxygen addition, sealing of uptakes, waste heat boilers and downstream ductwork is mandatory for efficient, minimum cost, SO_2 control.

The most extensive work performed to seal reverberatory furnaces specifically to facilitate SO_2 control has been conducted at the Onahama smelter in Japan. A direct quotation from Reference 15 clearly indicates the possiblities for the use of this technique as follows: "Air infiltration into the offgas, which had amounted to approximately 50 percent of the furnace exit gas at the uptake, was reduced to less than 15 percent by eliminating air leaks through crevices, clearances and openings of the furnace roof, sidewalls, fettling chutes, damper slots, expansion joints, peep holes, cleaning doors and especially dust discharging hoppers of the boilers and the Cottrell treaters."

Converter slag return, use of charge slingers or Wagstaff-type feeders, and slurrying repair of furnaces all contribute to excess air infiltration by requiring intermittent large openings. Infiltration of air around burners can be another bad offender when furnace pressure is not carefully monitored and regulated. Open cracks in refractory arches and sidewalls should be sealed as they develop.

At Onahama, the major leakage points in the reverberatory furnaces are at the two slag doors, the charge ports, the burner entry (eight burners), cracks, the oxy-fuel burner ports and the bath measuring ports. It is necessary to repair and replace portions of the furnace roof every 6 months to minimize leakage. This is particularly true within an area of approximately 10 meters long from the burner end.

The slinger charge system at Ajo tends to increase dilution because there is a fairly large door opening required. They have at times also cutoff the burners during charging in order to mininimize furnace gas dilution.

Slag return launders are generally near the furnace end. Also, it is possible to minimize the amount of infiltration air by mechanically closing the door while mechanically moving the slag return launder in and out. This is done at the new Morenci furnace.

In terms of space allowed between bricks, there has been as much as 100 mm (4 in) expansion allowed in 9 m (30 ft) length. When hot, the refractories theoretically expand and seal these openings. Proper maintenance is the major factor for minimizing leaks or infiltration air. Hand sealing of all cracks between refractories should be routinely practiced. With a silica arch, it is possible to spray on a repair, but the basic material cannot be patched in this manner.

Extensive sealing will, as mentioned, eliminate the cooling effect of infiltration air. The furnace must then be operated in such a way that overheating will not occur. In some cases it may be necessary to use a different refractory material or readjust burner location and operation.

Additional techniques to minimize air infiltration include straight through boiler design with air-sealed mechanized ash pit dust removal facilities, the use of permanently mounted steam soot blowers in boilers and flue systems (instead of hand lancing), and additional burners at strategic points in the flue system to melt accretions (instead of opening doors for hand cleanout). Periodic maintenance sealing of flues, precipitators, and treatment facilities is also required to prevent dilution of the SO_2 after passing through the furnace waste heat boilers and before it can be processed.

3.4 PRESSURE CONTROL

The general objective in the operation of the reverberatory furnace is to maintain a slight negative pressure (0.005 to 0.050 in. of water) throughout the furnace. This prevents gases from escaping through any openings and also brings in cooling air to reduce brick and metal temperatures at critical points. Of course, the lower the pressure, the greater will be the amount of air entering, resulting in greater fuel requirements with more SO_2 dilution.

It is common practice to use butterfly dampers in the ductwork downstream of the wasteheat boilers to automatically control the pressure in the reverberatory furnace. The butterfly type is more common although some sliding dampers are used.

Normally when charging occurs there is only one, or possibly two, charge pipes open at a time so that the pressure surge that accompanies the charging tends to be dampened out by the mass of gas within the system. Thus, high response pressure control systems have not been used. Draft controls normally have antihunting devices on them.

The operation that causes the greatest pressure fluctuation is the slag return and the slag return launder opening. The slag reacts with the molten material causing a more rapid gas evolution tending to increase pressure. The slag return opening tends to allow a major quantity of infiltration air to enter. Some smelters use this infiltration air to help cool the arch.

In the wet charge reverberatory where sloughing occurs from the charge banks, generation of gas can occur so rapidly that the relief openings are not sufficent to relieve the pressure. There have been occasions when the arch was blown off the furnace.

At Onahama, pressure control is set by a sensor just before the uptake which is connected to a damper downstream of the boiler. The control pressure is reset every week or so by observation of leakage out of the roof. Figure 3-1 shows the variation of pressure versus the length in the furnace. It indicates the potential for positive pressure at some points in the furnace even though most areas are negative. Location and maintenance of pressure sensors are of prime importance particularly since the peak pressure point may shift as furnace operating conditions change.

Close attention to the pressure setting can help minimize dilution air. It is effective regardless of the existing effective open area.

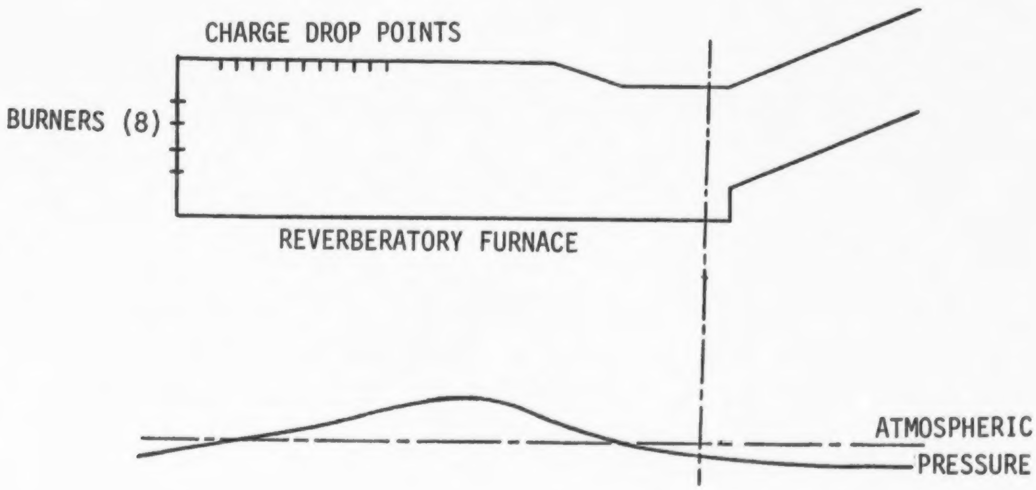


Figure 3-1. Pressure Variation Along Centerline of the Reverberatory Furnace at Onahama Smelter

3.5 PREHEATED AIR

Preheating furnace air can reduce the amount of additional burner energy required in the furnace with consequent reduction in nitrogen if indirect heating is used. This will reduce the amount of combustion-related gas and should, therefore, increase SO_2 concentration. Air is preheated to 400°C at the Onahama smelter and a 6 percent increase in SO_2 concentration results.

As indicated in Reference 16, using preheated air for natural gas combustion is usually required to increase flame temperatures thereby increasing heat transfer to the melt by radiation and convection. The use of preheated air for burning oils and pulverized coal accomplishes the same thing but can introduce furnace durability and control problems because of the higher temperatures encountered. Also, according to the above reference, fuel can be burned in a preheater with greater efficiency than in the furnace because of the much lower temperatures of waste combustion gases in the preheating operation.

Preheating air is common practice in the industry primarily for efficiency reasons. It is not expected that preheating will be used with oxygen enrichment (Section 3.9) because of the reduction of combustion air.

3.6 PRELIMINARY PROCESSING USING FLUID-BED ROASTERS

There are two exceptions to the general rule that the SO_2 concentration should be increased to facilitate its control. Assuming that all efforts have been made to reduce gas volume, the two approaches that make it desirable to reduce SO_2 concentrations are:

1. Neutralization forming a waste or throwaway product
2. No control

In the case of neutralization using for example, the lime/limestone gypsum system as presently practiced at the Onahama smelter reverberatory furnace in Japan (Section 5.2), the lower the quantity of SO_2 generated the less will be the input material lime or limestone required and the less will be the output gypsum to be handled and "thrown-away." In the case of no control, it is conceivable that if a small enough quantity of SO_2 is generated in the reverberatory furnace, it can be emitted and still allow the smelter to meet its ambient air quality requirements.

The one technique that results in reduced SO_2 from the reverberatory furnace without introducing additional pollution control problems in other portions of the smelter is the use of fluid-bed roasters. The fluid-bed roaster produces an offgas stream in the 8 to 18 percent SO_2 range and, by its nature, is usually a very well-sealed device with minimum fugitive emissions. This high SO_2 concentration can be readily controlled by separate processes.

It appears from the data in Reference 17 that reduced sulfur emissions from the reverberatory furnace result when a fluid-bed roaster is used for initial processing of the charge. The roaster allows the free atom of sulfur attached to the iron to be driven off easily. In addition, some of the combined sulfur is burned, iron is oxidized and heat is produced in the calcine which reduces the amount of fuel necessary in the reverberatory furnace to maintain temperature. The fraction of sulfur removed in the roaster depends on the composition of the ore, and the operating temperature of the roaster. To make matte with the chalcopyrite, the most sulfur that can be taken in the roaster is approximately 40 percent. With chalcocite it is possible to go to a complete dead roast, but this ore is not generally encountered in the United States to as great an extent as the chalcopyrite.

If green charge of good concentrate grade is used, matte grades between 30 and 36 percent result from the reverberatory furnace. This could be too low a grade, in many cases, to go to the converters. Ideal matte grade is 42 to 46 percent. Most plants add roasters because of very low concentrate grade or custom materials of varying grades and impurity levels.

The nature of the smelter feed and the economics involved are the prime considerations for determining whether the charge should be preroasted. The desired grade of matte is regulated by converter capacity and costs. The median copper range is between 40 to 45 percent.

When feed contains excess sulfur beyond the matte requirements, it is either necessary to remove excess sulfur by roasting or to add sufficiently to the converter capacity to treat the lower grade of matte that will be produced. The final decision depends upon the balance between the cost of roasting and the cost of converting.

The other factor that determines whether roasting is desirable is the possible need for production of sulfuric acid from roaster gases. This was the case in one Arizona smelter some years ago when a need for acid arose for a concentrator leach-precipitate-float treament. It was decided to install a fluid-bed roaster to make the partial roast on a portion of the smelter feed in order to produce high strength SO_2 to satisfy the acid requirement. Other reasons were to provide a rich SO_2 stream for direct acid plant processing to produce acid for emission control.

As high as 15 to 18 percent SO_2 concentration in the gas from fluid-bed roasters has been obtained, although in most cases 8 to 10 percent is normally achieved. This is ideal for making acid particularly since the roaster operates under continuous steady-state conditions required to feed the acid plant. Kennecott/Hayden converted to roasters to make acid in order to leach their silicate ore body. ASARCO aims for 42 percent matte so that some secondaries can be handled in the converters. Another advantage for roasting is that with calcine feed into the furnace, fuel consumption and gas volume are reduced by approximately 30 to 40 percent, as compared to green feed. This is due primarily to the preheating energy introduced into the furnace by the hot calcine. In addition, from 6 to 11 percent of the concentrate is water. This, of course, is removed in the roaster, although this could be a disadvantage if the water is required in a subsequent SO_2 control system (refer to Section 5.0).

While it appears that the current philosophy in the copper industry is to use fluid-bed roasters, some circumstances exist that will not allow their use. Sufficient grinding is needed to liberate values. However, with underground ores where mining results commonly in large pieces compared to smaller sizes for open pit, it is sometimes necessary to reduce the size so much that the grinding cost would be excessive. In rare cases ores are directly smelted without concentrating. Ores with a 4-1/2 percent copper reduction have been directly smelted without concentrating. There may also be an increase in magnetite formation depending upon the composition of the charge. A low grade matte (more easily controlled with multi-hearth roasters) may be required for subsequent converter lead elimination.

The use of fluid-bed roasters may be undesirable when arsenopyrites are present. Antimony, bismuth, and selenium may also cause problems. These impurities are relatively difficult to separate by volatilization, and a fluid-bed roaster may not provide sufficient residence time for complete separation. Multi-hearth roasters, on the other hand, provide a much longer residence time as the ore travels through each hearth - up to 11 in all. Experience has shown, however, that bismuth is not usually a problem in U.S. smelters, and arsenic and antimony, if present in the product, can be removed in the anode furnace. Anaconda, processes ores containing nearly 1 percent arsenic with a fluid-bed roaster. Furthermore, multihearth roasters tend to produce greater fugitive emissions.

If residence time is a problem, it is possible to use a three-stage fluid-bed roaster. The first stage is the drying stage which could be fluid-bed drying or any other drying device such as a rotary kiln. This would then be followed by two stages: one with an oxidizing atmosphere and another with a neutral or reducing atmosphere. Lurgi apparently does this with arsenopyrite. Also, this technique was used for gold ore processing.[18]

3.7 OPERATION AT LOWER AIR-TO-FUEL RATIO

The quantities of primary and secondary air allowed to mix with fuel in burners can control gas temperature and gas combustion to a limited extent. If the amount of carbon, sulfur, and hydrogen in the fuel is combined with the exact amount of oxygen to complete their combustion to CO_2, H_2O, and SO_2, then the theoretical amount has been supplied. Usually, for most common combustion devices, an excess of oxygen is used to ensure efficient fuel useage.

The point of efficient (most economical) combustion has been passed when the heat lost to the dry gases from the additional air (supplying the oxygen) exceeds the heat gained from the combustion of any additional fuel. As gas is easily mixed with air, it is the easiest fuel with which to obtain complete combustion. Commercial burners are available which can operate with 0 to 10 percent excess air, still obtaining complete combustion. Liquid fuels are less easily mixed with air, so they require up to 18 percent excess air. Solid fuels require from 12 to 50 percent excess air and sometimes leave unburned carbon in the ash residue. With a given amount of sulfur oxidized in the furnace, the SO_2 concentration will increase as oxygen (air) is reduced. The air is supplied by burner primary and secondary air and air infiltration through the various leakage points (Section 3.3). The burner design and its burning efficiency will govern the amount of excess air required introducing a counter-balancing effect.

It is indicated by the analysis of the furnace operation at Onahama (Appendices E and F) that underfiring or operating at less than theoretical air at the burner end of the furnace and operating overall with no more than 10 percent excess air (not considering iron oxidation) can increase the SO_2 concentration. While green charge furnaces are emitting 1.5 percent SO_2 average in the U.S., the Onahama smelter, emits 2.6 percent SO_2 average. The effects of the additional sealing efforts at Onahama, of course, also promote the higher value.

It is known that the Onahama furnace designer intended for the furnace to operate more fuel rich than normal U.S. practice. While this does not provide a maximum heat release in the furnace, in addition to high SO_2 concentration, it does increase furnace durability and also reduced NO_x formation. Originally, 500 ppm NO_x

resulted when operating on the oxygen-rich side. When the air-fuel ratio was reduced to the fuel-rich side, the NO_x dropped to 100 ppm.

One possible side effect of more fuel-rich operation may be the distillation of sulfur which does not encounter oxygen in the furnace. The distilled sulfur acts like cement when combined with the dust and can cause flue plugging and possible precipitator operating problems.[19]

3.8 INSTRUMENTAL CONTROL OF REVERBERATORY SMELTING

The fact that copper smelting is an art and not a complete science has been firmly established through the years. Nevertheless, partial control by computer is entirely possible for about 90 percent of the process and is feasible if human judgement is retained. With the advances in sensing and measuring instrumentation in recent years, it is desirable that these be employed as far as possible to level out reverberatory operations.[20]

Of particular importance is the monitoring of temperatures and gas composition throughout the furnace; maintenance of constant draft conditions through activated multiple dampers; automatic but also controlled charging, as needed, along furnace smelting areas; monitoring of bath depth throughout the furnace; complete combustion analysis of furnace gases at different points in the furnace and at outlet; fettling of bridge wall and front end of furnace as needed; and visual monitoring of furnace interior, thereby allowing the human judgement factor when required. Proper use of instrumentation will dictate the need for specific furnace sealing, burner adjustment (including flame length and direction), rate of charging in certain areas, need for fettling, patching, flux additions, oxygen balance, etc. Prime drawback to instrumental use for full control is inability to instantly analyze matte, slag, and gases, as well as to determine weights and measure flows. Most smelters use some instrumentation and automatic controls. However, time response and system maintenance varies from smelter to smelter.

A more constant operation of the reverberatory furnace can contribute to lower operating costs, as well as more stable and high SO_2 concentrations.

3.9 OXYGEN ENRICHMENT

3.9.1 INTRODUCTION

Conventional air-fuel burners cannot match the efficiency of oxygen-fuel combustion. The air used in conventional burners is four-fifths nitrogen, which does not contribute to the combustion process. Nitrogen robs the flame of heat that could increase production. Nitrogen not only chills the flame, but also vents useful heat to the stack. Saddington et al [21] report that about 45 percent of the gross thermal input in an air-fuel fired reverberatory furnace leaves as sensible heat in the nitrogen. The amount of heat carried away by each ton of nitrogen is of the same magnitude as that required to smelt 1 ton of solid charge. Oxygen-enriched fuel combustion increases furnace efficiency, flame temperature, and flame propagation over air-fuel. Immediate fuel savings are an obvious advantage. But oxygen usage may also allow a smaller furnace to do the same job, or the same furnace to do more work because convective heat transfer efficiency is increased. Higher heat and flame temperature also increase process reaction rates, or reduce melt-down time.

Oxygen has been used for a number of years to markedly intensify metallurgical processes. It has been accepted and used in converters in the nonferrous smelting industry. But the industry in the U.S. seems hesitant to use oxygen in reverberatory furnaces even though it has been proven elsewhere that it would increase production, and decrease fuel consumption. An additional effect found to result from oxygen enrichment was an increased SO_2 concentration in the flue gases. As a result of increasing fuel costs, the present trend is toward optimizing fuel usage.

While most of the work on oxygen enrichment to date has been done to achieve increased production, an increase in SO_2 concentration has been demonstrated, in the flue gas stream.

It should be noted that the extent of the increase in SO_2 concentration will be dependent upon several factors including furnace feed, chemical constituents, extent of preprocessing, dilution air and general operating conditions. The furnace charge composition can determine the availability of sulfur for SO_2 formation under furnace operating conditions as discussed in Section 2.3.3.3. This can then set the level of effectiveness of the oxygen enrichment technique.

The advantages of oxygen enrichment in a reverberatory furnace have been emphasized by numerous authors.[21-78] The most extensive gain in SO_2 concentration was obtained with a green charge reverberatory furnace in Chile where values as high as 5 percent were attained. The basic principle involved in oxygen enrichment is to decrease the quantity of nitrogen. The nitrogen is inert and consumes energy which cannot be utilized in the smelting process. The oxygen in a reverberatory furnace is used for combustion and metallurgical processing. Each of these activities are discussed in detail in succeeding paragraphs.

3.9.2 OXYGEN UTILIZATION IN A REVERBERATORY FURNACE

Various methods of oxygen introduction to the reverberatory furnace have been used to date. They are as follows:

1. Oxygen-fuel burners - oxygen is introduced directly with fuel in separate burners.
2. Oxygen mixed with primary or secondary air and introduced into the existing burner system.
3. Undershooting the flame with oxygen or oxygen-enriched air.
4. Oxygen lancing of the molten charge.

Itakura et al [22] and Goto [23] report using oxygen-fuel burners that penetrate the furnace roof vertically at the Onahama Smelter and Refinery. Eastwood et al [24] report using oxygen-enriched primary air in the burners at the Rokana Smelter. Pluzhnikov et al [25] report oxygen-enrichment of primary air in burners at Noril'sk Ore-Mining Combine. Kupryakov et al [26] report using oxygen-enriched primary air in burners at the Almalyk Copper Smelter. Saddington et al [27] report using oxygen-enrichment in combustion air at INCO Smelting for copper-nickel ore. Wrampe et al [28] report Linde's experience with oxygen-enrichment of combustion air in reverberatory furnaces at U.S. smelters. Beals et al [29] have a patent assigned to Kennecott for using oxygen lancing of the melt to increase production and to obtain high SO_2 concentration in the flue gases. Further discussion on oxygen injection techniques is included in Section 3.9.3.

Zhuravlev et al[30] report the effect of fuel rate and oxygen-enrichment on thermal absorption into the charge. The thermal absorption along the length of the reverberatory furnace is shown in Figure 3-2 for the conditions of (1) normal operation (no oxygen addition), (2) increased fuel rate (no oxygen addition), and (3) oxygen-enrichment (normal fuel rate).

The combustion process is based on two mechanisms - heat transfer and mass transfer. Heat has to be transferred to the fuel to vaporize fuel (assuming oil) which then combines with oxygen. If the mixture is held at or above the ignition temperature, the mixture is ignited. So, in order for this process to function properly, there should be enough heat for the fuel to vaporize or gasify, enough oxygen to diffuse and combine with the fuel vapor, and the mixture should be maintained at or above the ignition temperature.

From the results of Zhuravlev et al[31], it is seen that when the fuel rate is increased in a regular burner, the flame length increases and the flame temperature is reduced near the burner end although it increases in the latter part of the flame. Because

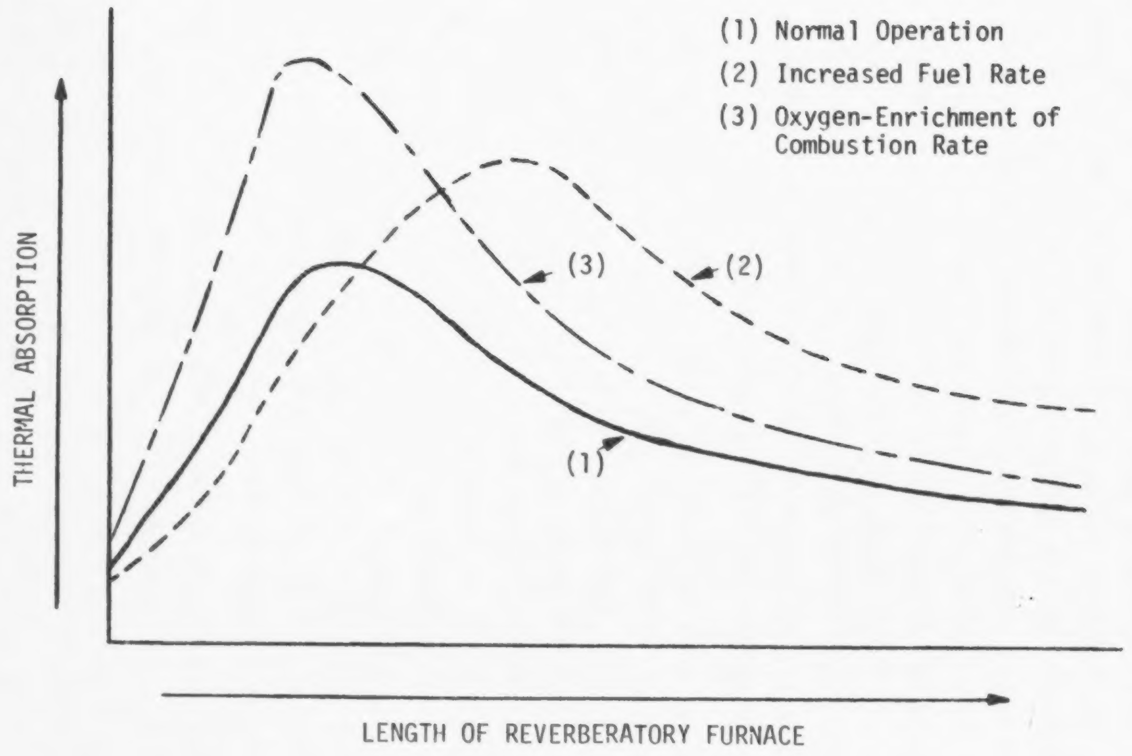


Figure 3-2. Thermal Absorption Along the Length of the Reverberatory Furnace For Normal Operation Conditions, Increased Fuel Rate, and Oxygen Enrichment

of the larger volume of fuel involved, the mixture of fuel and air is fuel-rich and oxygen diffusion is limited in the first part of the burner. This results in a lesser quantity of fuel burning near the burner with a reduced heat release in this area. A large portion of the heat evolved is used in vaporizing the fuel, and little heat is available to maintain the mixture at ignition temperature, thereby decreasing the burning rate. By the time the flame travels a small distance into the furnace, most of the fuel is vaporized. Then, there is an adequate mixture of fuel and air so that the flame is no longer diffusion limited. Since there is a large amount of fuel present, once the combustion starts, and the flame is no longer diffusion limited, a large amount of heat is released and the temperature of the flame increases rapidly. This continues until all the fuel has been used.

The temperature of the flue gas leaving the furnace increases with an increase in fuel rate (if in excess of charge requirements), thereby more and more sensible heat is lost in the flue gas resulting in higher specific fuel consumption. Specific fuel consumption is defined as heat (BTU) of fuel required to smelt a ton of charge in the reverberatory furnace. With an increase in fuel rate, even though the flame temperature near the burner end is decreased, the heat absorption increases in this section due to the longitudinal radiation. The heat transfer rate to the feed also increases with increasing fuel rate, due to the overall increase in the furnace temperature.

When combustion air is enriched with oxygen, the flame length decreases, the flame temperature is higher near the burner end, and the furnace temperature tends to increase. After enriching the combustion air with oxygen, the flame in the first part of the furnace is not oxygen diffusion limited as in the case of increased fuel rate, it is only heat transfer limited. Once the fuel starts burning, enough heat is generated to vaporize the fuel and maintain the fuel oxygen mixture at ignition temperature. Since the flame is not oxygen diffusion limited, the fuel ignites faster, and the burning process is escalated producing high temperatures. The flame length decreases because all the fuel is burned in a short time due to higher oxygen diffusivity and better heat transfer. Owing to the decreased inert nitrogen concentration in the furnace air, for a given quantity of fuel burned, the furnace air can be heated to higher temperatures when combustion air is enriched with oxygen. Furthermore, while the fuel burns faster, a greater amount of disassociation occurs keeping maximum temperatures low as well as maintaining temperature for a longer length of time due to reassociation (see Figure 3-7).[32]

From a heat transfer point of view, having higher flame temperatures at the burner end is very desirable because (1) this will increase the thermal absorption, and (2) maximum quantity of heat will be absorbed before the gases leave the furnace, thereby optimizing the fuel usage.

Chizhikov reports that the smelting process is not chemical reaction limited, but it is heat transfer limited. The objective is to have maximum heat transfer to the feed at minimun cost.[33] Both higher fuel rates and/or oxygen-enrichment would give higher heat transfer rates to the feed. With higher fuel rates since the flame temperature is very high in the latter part, the furnace gas temperature is increased in this section increasing the heat transfer due to conduction and convection. Also the higher flame temperature with its higher emissivity increases the radiant heat transfer.

The flame is shortened with oxygen-enrichment, and since all the fuel is burned in a shorter time, the furnace gas temperatures increase. This increase in furnace gas temperature increases the heat transfer to the feed by conduction and convection. The increased flame temperatures also increase the radiant heat transfer. Since most of the heat in a reverberatory furnace is required in the earlier stages of the furnace where the cold charge has to be melted and maintained at a sufficient temperature for the chemical reactions to occur, it is very desirable to have flame characteristics similar to that obtained with oxygen-enrichment. In the latter parts of the furnace, the furnace gases only have to be maintained at a high enough temperature to assure that the matte and slag remain molten at a sufficient temperature to facilitate separation.

Wrampe et al [34] report that higher furnace operating temperatures might create a slag handling problem due to its decreased viscosity. However, this can be alleviated by an appropriate addition of silica flux in the feed.

Beals et al [35] report using oxygen in a reverberatory furnace to increase production by using oxygen-riched air for bath agitation by lancing the bath. The benefits of using this method are: better heat transfer to the fresh feed piles by the splashed molten material (conduction), radiant heat transfer from the molten material splashed on the furnace walls, and direct transfer to both matte and slag by the splashing thereof into the combustion flame and gases.

Goto[36] points out that a somewhat different heat transfer mechanism occurs using separate oxygen-fuel burners that direct the flame on the charge banks in the Onahama furnace. The purpose for using the burners was to take advantage of the release of heat when CO_2 and H_2O are reassociated. The dissociation of these molecules in the 2,000° to 2,900°C temperature range absorbs heat which is released when gases are cooled. By applying the flame directly to or near the charge piles in the reverberatory furnace, the reassociation heat which is released is applied directly to the material to be smelted. The heat of dissociation consumed by the dissociation of CO_2 and H_2O account for approximately one-half of the total calorific value of pure oil. When the flame comes in contact with low temperature material, the reaction heat is released by reformation of CO_2 and H_2O. The rapid smelting of concentrate is possible because of direct application of the flame to charged material banks. It is believed that this method of oxygen utilization is more efficient than simple oxygen-enrichment of combustion air. However, improper application could cause serious adverse effects on thermal efficiency.

3.9.3 METHOD OF OXYGEN INTRODUCTION TO THE FURNACE

To date, various methods of introducing oxygen to the furnace have been successfully tested. These include oxygen-rich air lancing of the bath, oxygen-fuel burners that penetrate the furnace roof and are directed towards the charge banks, use of oxygen jets next to the regular burners, undershooting of the flames with oxygen, using oxygen lances across the furnace just above the bath, and enriching the primary combustion air with oxygen, etc. Sketches of these methods of oxygen introduction in a reverberatory furnace are given in Figures 3-3a through 3-3f.

According to experts in oxygen application in furnaces, enrichment of primary combustion air with oxygen is perhaps the easiest method of introducing oxygen in the reverberatory furnace, but it is also the least effective way of utilizing oxygen. Oxygen utilization can be improved by undershooting the flame with oxygen, but this method is difficult to control. Perhaps one of the best methods of oxygen utilization in a reverberatory furnace is the use of oxygen-fuel burners, such as those used at Onahama. They are easier to control and utilize the oxygen very efficiently. Further expansion of this technique was used at the Caletones smelter in Chile where all fuel was burned with pure oxygen in oxygen-fuel burners.

The fraction of heat input into the reverberatory furnace which is absorbed by the charge in a normal operation without oxygen-enrichment is approximately 25 percent. With the oxygen-enrichment of primary combustion air or undershooting of the flame with oxygen, the fraction of heat utilized for actual smelting is increased to nearly 30 to 40 percent. When oxygen-fuel burners are utilized in a reverberatory furnace, the heat utilization for smelting is considerably higher. This is caused by disassociation and reassociation effects. This method has been extended at the Caletones smelter to include total fuel injection

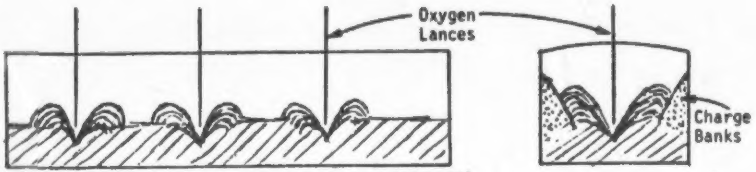

Oxygen Lances
Charge Banks

Figure 3-3a. Oxygen Lancing of the Bath (Ref. 29)

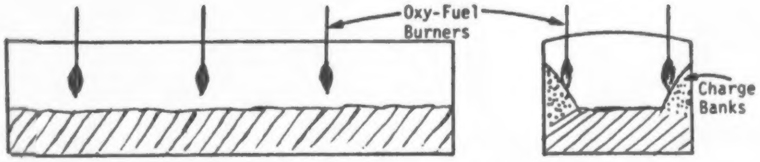

Oxy-Fuel Burners
Charge Banks

Figure 3-3b. Oxygen-Fuel Burner Usage in the Furnace (Ref. 25,36, and 37)

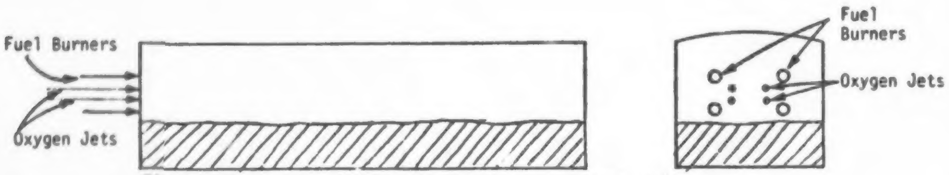

Fuel Burners
Oxygen Jets
Fuel Burners
Oxygen Jets

Figure 3-3c. Use of Oxygen Jet Next to Burners (Ref. 24)

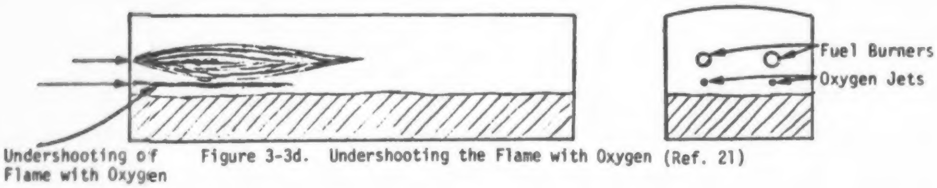

Fuel Burners
Oxygen Jets
Undershooting of Flame with Oxygen

Figure 3-3d. Undershooting the Flame with Oxygen (Ref. 21)

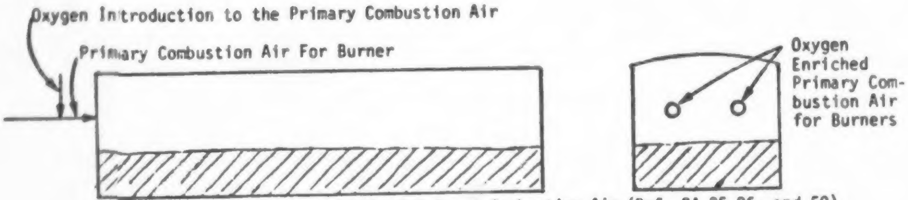

Oxygen Introduction to the Primary Combustion Air
Primary Combustion Air For Burner
Oxygen Enriched Primary Combustion Air for Burners

Figure 3-3e. Oxygen-Enrichment of Primary Combustion Air (Ref. 24,25,26, and 50)

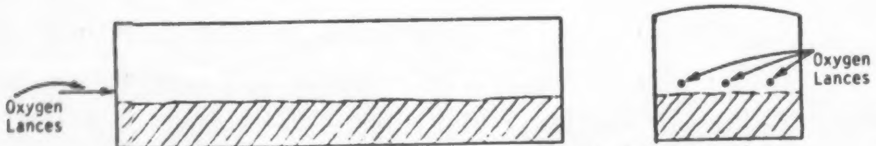

Oxygen Lances
Oxygen Lances

Figure 3-3f. Horizontal Oxygen Lancing just above the Bath (Ref. 28)

Figure 3-3. Methods of Oxygen Addition

through a multiplicity of oxygen-fuel burners resulting in high SO_2 concentration and fuel efficiency.[37]

The experiences with the above methods are discussed in the following sections of this report.

3.9.4 EXPERIENCE WITH OXYGEN-ENRICHMENT

Saddington et al[38] of INCO describe how oxygen-enrichment of the combustion air affected either a reduction in the coal consumption by 19 percent or increased the production by 36 percent when smelting copper-nickel concentrates. Their test results are given in Table 3-1.

Table 3-1. INCO'S DATA ON OXYTEN ENRICHMENT IN A REVERBERATORY FURNACE

OXYGEN-ENRICHMENT	TEST	STANDARD
Coal rate, tpd	174	214
Oxygen rate, tpd	91	Nil
Net matte and slag, tpd	1,540	1,400
HIGHER THROUGHPUT RATE WITH OXYGEN-ENRICHMENT		
Coal rate, tpd	213	206
Oxygen rate, tpd	80	Nil
Net matte and slag, tpd	1,900	1,400

Kupryakov et al [39] report Russian experience with oxygen-enrichment of combustion air at Balkhash Mining and Metallurgical Combine. [31] Their test results show that with each percentage of airblast enriched with oxygen, reverberatory performance increased by 2.7 percent, while fuel consumption dropped by 2.2 percent. Sulfur dioxide concentrations in the waste gases increased from 1.5 to 2.5 percent, while the amount of dust entrained with the waste gases fell by 40 to 45 percent. The wear of the brick lining of the furnace arch, with oxygen-enriched blasts fed to the air duct, was the same as when conventional airblasts were used.

Kupryakov et al also report the tests conducted at Almalyk Copper Smelter on the use of oxygen-enriched blasts in reverberatory smelting in order to find optimum methods of feeding oxygen to the furnace.[16] Increasing the oxygen content in the blast from 21 to 40 percent brought an 84.4 percent increase in the furnace output capacity. Figure 3-4 shows the variation in specific fusion* with the oxygen content of a blast and its growth per 1 percent of oxygen addition of the blast.

The SO_2 concentration was measured at varying operating conditions for the furnace. Waste-gas samples for determining the SO_2 content were taken at the furnace output. The SO_2 concentration in the flue gas sharply increased up to 25 percent O_2 in the blast as shown in Figure 3-5. Beyond this oxygen concentration in the blast, the SO_2 concentration in the flue gas slowly flattens. Increasing the oxygen content of the blast from 21 to 40 percent, increased the SO_2 concentration in the flue gas from 2.4 to nearly 7 percent.

Zhuravlev et al[41] did some theoretical work on the smelting rate in a reverberatory furnace with oxygen-enrichment of combustion air. They give a nomograph for specific fusion in a reverberatory furnace as a function of fuel rate and percent of oxygen-enrichment. Figure 3-5 is the nomograph which shows the dependence of the specific fusion of the charge on the thermal load (fuel rate) at various O_2 content in the blast. It was stated that the model was verified at NGMK Copper Smelter. Their tests show the direct relationship between the smelting rate, fuel rate, and percent of oxygen-enrichment of the combustion air.

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*Specific fusion - Tons of charge smelted per square meter of furnace hearth per day.

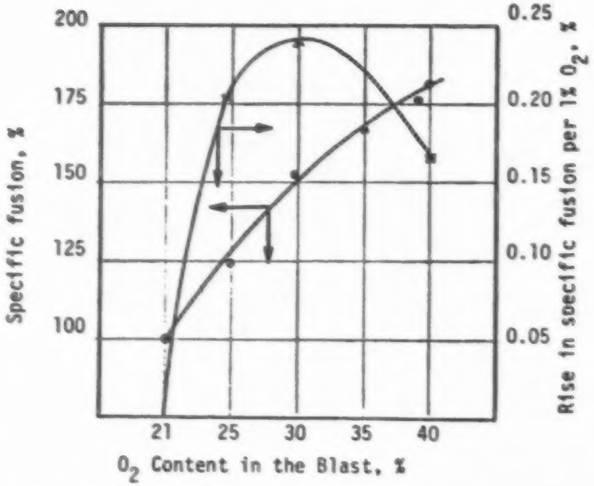


Figure 3-4. Variation in Specific Fusion with Oxygen Content of a Blast and its Growth per 1% of Oxygen addition to Blast

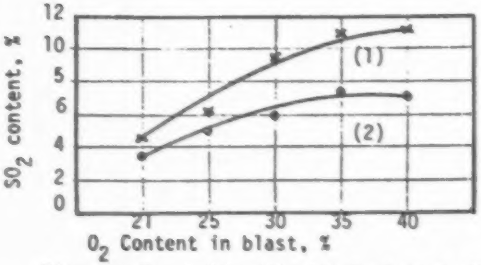


Figure 3-5. Sulfur Dioxide Content in Waste Gases From the Reverberatory Furnace as a Function of the Oxygen Concentration in the Blast

(1) - Calculated
(2) - Experimental

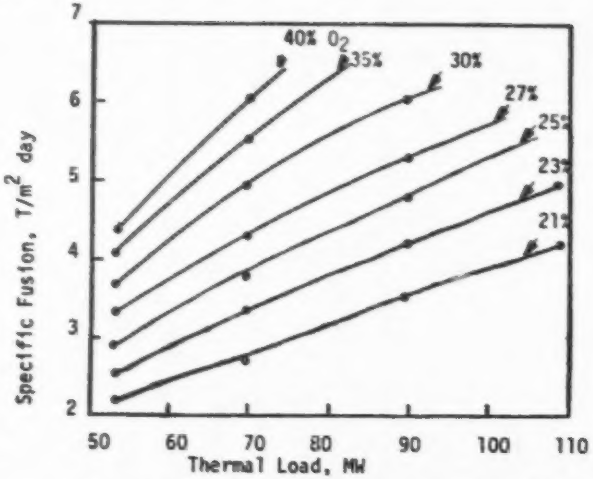


Figure 3-6. Dependence of the Specific Fusion of the Charge on the Fuel Rate at Various O_2 Content in the Blast in Reverberatory Furnace

Wrampe el al [42] report Linde's experience with oxygen-enrichment of combustion air in reverberatory furnaces at U.S. smelters. They came up with a mathematical model of the copper reverberatory furnace. The model describes the smelting, flue gas rates, and the effluent SO_2 concentrations as functions of the tonnage oxygen and fuel rates. The model was verified at various smelters in the U.S. Their theoretical and experimental results indicate that when fuel rate was increased with oxygen usage, the incremental charge-to-oxygen ratio was ascertained to range between 4.5 to 7.0 tons per ton. The SO_2 content of the effluent gas was increased from 3.5 to 5 percent with oxygen use. Copper losses in the slag diminished by 15 to 23 percent. Generally, it was found that the overall refractory and material temperatures increased by approximately 0.5 F° per mscfm of oxygen and the flue gas temperature increased by about 1.2 F° for the same amount of oxygen.

Itakura et al [43] report their experience with oxygen-fuel burners that penetrate the furnace roof vertically and are directed towards the charge banks at Onahama Smelter. The oxygen consumption was 2,370 m^3/hr (83,700 ft^3/hr). The advantage of using the oxygen-fuel burners that penetrate the furnace roof vertically is that the heat is released near or on the charge banks rather than near the furnace lining thereby eliminating the problem of exceeding the lining temperature limitations.

Goto [44] further describes the experience at the Onahama smelter. A pilot furnace of 120 ton solid charge per day capacity was used to conduct oxygen-enrichment experiments. These tests were conducted to determine the optimum conditions for the most efficient combustion.

The experiments were continued over a period of 3 years. The results showed that the formation of dust, the oxidation of sulfur, and the matte grade are comparable, under appropriate conditions, to those in a conventional green charge reverberatory operation. Wear of the furnace refractories was also found not to be serious and it was confirmed that the oxygen-oil burner can be successfully applied to the reverberatory furnace.

The oxygen-oil burner used for these experiments was developed by Shell Research Limited and was somewhat modified to establish its suitability for smelting of copper concentrates.

In 1971, the oxygen-oil burners were installed in addition to the existing conventional oil burners in the full-scale reverberatory furnace. Table 3-2 shows the general specification of the oxygen-oil burner. Two burners were used and are presently being used when furnace capacity must be increased. Table 3-3 shows the reverberatory furnace data before and after the use of oxygen-fuel burners in the furnace. Capacity has been increased by 3,000 tons of concentrates per month for each burner at an equivalent oxygen concentration in the reverberatory furnace of 22.5 percent (in the air). The exhaust gas volume has remained the same and relatively little refractory wear or slag loss has been encountered.

Table 3-2. GENERAL SPECIFICATIONS OF THE OXYGEN-OIL BURNER AT ONAHAMA SMELTER

Fuel	Bunker C oil
Fuel consumption (max.)	106gal/Hr
Oxygen consumption (max.)	42,400ft^3/Hr
Oxygen pressure	71 Lb/in^2
Length	76 in
Diameter	6 in
Cooling system	Water Jacket

Table 3-3. REVERBERATORY FURNACE DATA AT ONAHAMA SMELTER BEFORE AND AFTER THE USE OF OXY-FUEL BURNERS IN THE FURNACE

	Dec. 1970	Jan. 1972
Concentrate smelted (ton)	24,769	29,919
Silicious flux smelted (ton)	3,279	4,038
Limestone smelted (ton)	2,059	2,171
Reverts smelted (ton)	571	779
Total solid charge (ton)	30,678	36,907
Fuel oil consumed (kl)	4,723	4,870
Oxygen consumed (stp cu m)	-	667,058
Matte produced (ton)	20,354	25,180
Matte grade (%)	34.5	34.4
Slag produced (ton)	20,443	25,936
Copper in slag (%)	0.46	0.47

Note: All weights are on dry basis.

Eastwood et al [45] report their experience with oxygen-enrichment at the Rokana smelter. The oxygen consumption at the reverberatory furnace was 90 ton per day. An 18 percent increase in production resulted, which was far below expectations. The performance was later improved by optimizing the oxygen injection. The SO_2 concentration in the flue gas stream increased from 1.0 to 1.6 percent.

Vera et al [46] and Achurra et al [47] present the experience using oxygen-fuel burners at the Caletones smelter in Chile. During a 5-year period, the smelter was converted from conventional end-burner air-fuel combustion to complete oxygen-fuel combustion using a maximum of 12 oxygen-fuel burners suspended from the roof impinging on the charge banks. Oxygen consumption reached 380 long tons per day. This allowed a smelting rate of 1,520 dry tons per day with a fuel consumption in the range of 0.81×10^6 Kcal. This was a considerable increase in production, which was the objective of the application, and also resulted in reduced fuel consumption. In addition, and most significantly from a pollution control standpoint, the SO_2 concentration range in the offgases increased to 5.8 to 7.3 percent. Oxygen-enrichment, under these conditions was approximately 60 percent with infiltration air providing nitrogen dilution. (See Appendix J for a more detailed discussion of the Caletones smelter experience with oxygen-enrichment.)

Smirnov's [48] heat engineering computations show the possibility of greatly reducing fuel consumption and of intensifying the smelting process when it is enriched with oxygen. Based on approximate calculations, the effect of oxygen-enrichment of air on fuel consumption is given in the Table 3-4.

Table 3-4. SMIRNOV'S COMPUTATIONS SHOWING THE EFFECT OF OXYGEN-ENRICHMENT OF AIR ON FUEL CONSUMPTION

O_2 CONTENT IN BLAST (%)	FUEL CONSUMPTION (%)
21	100
25	74
30	59
35	52

Smirnov[49] reports that calculations and test made at various plants show that when using blast containing 28 to 30 percent oxygen, the SO_2 in the reverberatory furnace gases is near 4 percent. Preheating blasts and enriching them with oxygen will intensify the smelting process and, according to approximate calculations, make it possible to increase the specific fusion in the reverberatory furnaces from 6-8 to 10-12 tons of charge per m^2 of hearth area per day when smelting roasted materials: it would be increased from 4-5 to 6-8 tons per m^2 if dried unroasted materials were being smelted.

Otvagina et al [50] report a study made on the composition of waste gases from the reverberatory furnace at the Almalyk Mining and Metallurgical Combine with a view of determining the possibility of using waste gases for sulfuric acid production. The reverberatory furnace output ranged from 4.5 to 6.5 ton/m^2 day depending on the blast oxygen content (furnace hearth area 240 m^2). During the study, a complete analysis was made of the waste gas composition by taking samples immediately downstream of the furnace. The temperature at the end of the furnace fluctuated from 1,250°C to 1,340°C, and the negative pressure was 0.2 to 0.55 mm H_2O. The technological characteristics for the reverberatory smelting operation are given in Table 3-5.

Table 3-5. REVERBERATORY SMELTING PROCESS CHARACTERISTICS AT ALMALYK MINING AND METALLURGICAL COMBINE

Oxygen content in blast (%)	Heat load of gas 10^6 Kcal/hr	Smelting rate ton/m^2 day	SO_2 in flue gas (%)
21	67.2	4.57	1.74
25-27	64.5	5.55	4.4
29-30	55	5.8	5.3

3.9.5 COMPARISON OF VARIOUS STUDIES IN THE LITERATURE

The results from Linde's model[51] were compared with Zhuravlev's model[52] and they were found to be in agreement. Two comparisons were made; the first with a constant fuel rate (natural gas) and increase in oxygen content of combustion air from 21 to 23 and 25 percent; the second with the fuel rate increased and the oxygen content of combustion air varied (21, 23, and 25 percent). The percentage increase in smelting rate was calculated for a base-case. The base-case conditions were 200 mscfh of natural gas and 21 percent oxygen in combustion air (no oxygen-enrichment).

For a constant fuel rate of 200 mscfh of natural gas, the percentage increase in smelting rate from the base-case conditions with 23 and 25 percent oxygen content in combustion air for Linde's model was 13.22 and 27.27. Zhuravlev's model gave the percentage increase in smelting rate as 14.6 and 28.75.

When the fuel was increased to 230 mscfh of natural gas, the percentage increase in smelting rates from the base-case conditions, with 21 and 25 percent oxygen content in combustion air for Linde's model were 23.55, 36.8 and 51.24. Zhuravlev's model gave the percentage increase in smelting rates as 14.6, 35.2 and 50.2.

Kupryakov et al [52] and Otvagina et al [54] report that the specific fusion in a reverberatory furnace increases 25 percent when the oxygen content in the combustion air is increased from 21 to 25 percent. This was found to be in good agreement with Linde's and Zhuravlev's models which gave the percentage increase in specific fusion as 27.27 and 28.75 percent, respectively. These references do not report the effects on matte grade or impurity elimination.

3.9.6 RELATIONSHIP BETWEEN OXYGEN-ENRICHMENT AND SO_2 CONCENTRATION IN THE FLUE GAS SYSTEM

The increase in SO_2 concentration in the flue gas stream with oxygen-enrichment to the reverberatory furnace can be attributed to a reduced quantity of gases generated. For a given stoichiometric oxygen-to-fuel ratio, the amount of flue gas per ton of material smelted decreases with oxygen-enrichment. Assuming that the amount of sulfur oxidized remains the same, the concentration of SO_2 in the flue gas stream increases with the decrease in the volume of flue gas. The nitrogen that would normally have been carried along with air oxygen is eliminated.

All the theoretical and experimental studies on oxygen-enrichment in reverberatory furnaces show that the SO_2 concentration in the flue gas stream increases with oxygen-enrichment. The relationship between SO_2 concentration in the flue gas stream with oxygen-enrichment given by Linde's model and Kupruakov's results were compared and were found to be in reasonable agreement. For example, at a constant fuel rate, with 21 and 25 percent oxygen content in combustion air, Linde's model gave the SO_2 concentration in the flue gas as 3.55 and 5.5 percent, respectively. Kupryakov's results gave the SO_2 concentrations as 3.8 and 5.8 percent, respectively. Table 3-6 compares the results of these two studies.

Table 3-6. LINDE'S AND KUPRYAKOV'S EXPERIMENTAL AND THEORETICAL DATA SHOWING THE DEPENDENCE OF SO_2 CONCENTRATION IN REVERBERATORY FLUE GAS ON OXYGEN IN BLAST

	% SO_2 in Flue Gas	
% Oxygen in Blast	Linde	Kupryakov
	Experimental	
21	3.1	3.8
23	3.75	---
25	4.6	5.8
	Theoretical	
21	3.6	4.1
23	4.35	---
25	5.3	6.3

With 30 percent oxygen content in combustion air, the SO_2 content in reverberatory flue gas at the Rokana smelter increased from 1.0 to 1.6 percent. At the Onahama smelter, the SO_2 strength in the flue gas increased by 0.3 percentage points of SO_2 per burner. The maximum oxygen consumption per burner was 1,190 m^3/hr (42,000 ft^3/hr). Onahama comparative results gave an increase from a concentration of 2.6 percent SO_2 with no oxygen, to 3.2 percent SO_2 with 22.5 percent oxygen content in the air.

Otvagina et al [55] report that when oxygen content in the blast was increased from 21 to 30 percent, the SO_2 concentration in the reverberatory flue gases increased from 1.47 to 5.3 percent.

Beals et al [56] report SO_2 concentration as high as 18 percent with oxygen lancing of the bath. The measurements were done on a pilot furnace using oxygen. It is believed that operating conditions in the furnace, the charge constituents, and the method of oxygen addition all influence the absolute value of SO_2.

The work at the Caletones smelter [57] indicated that with approximately 60 percent oxygen-enrichment (infiltration air providing nitrogen), an SO_2 concentration of over 7 percent could be attained with a full-scale working reverberatory furnace.

3.9.7 ADVANTAGES OF USING OXYGEN-ENRICHMENT IN REVERBERATORY FURNACE

The advantages of using oxygen-enrichment in reverberatory furnace are listed below and are discussed later in the same order.

1. Increase smelting rate
2. Decreased specific fuel consumption
3. Smelting of higher melting point materials
4. Reduced copper losses in slag
5. Decreased dust content in flue gases
6. Lower capital and operating costs of the flue gas handling systems
7. Increased SO_2 concentration in flue gas

There are indications that there is a net energy saving even including energy required for oxygen production.

As described earlier in this report, the smelting rate increases with oxygen-enrichment. Rokana [58] smelters achieved better than 18 percent increase in production with oxygen-enrichment. Linde reported a 25 to 50 percent increase in production with oxygen-enrichment. INCO [59] achieved a 36 percent increase in production with oxygen-enrichment. Kupryakov [60] reported that at a constant fuel rate, enrichment of the blast air to 35 percent increased the specific throughput by 64 percent.

Oxygen can be employed to reduce fuel and air rates while maintaining a constant smelting rate. Kuprayakov reports a decrease in fuel consumption by 2.2 percent with a 2.7 percent increase in production when oxygen was used in a reverberatory furnace at Almalyk Copper smelter. With oxygen-enrichment, INCO[61] received a decrease in coal consumption by 19 percent.

Since higher temperatures could be attained by using oxygen-enrichment due to more efficient combustion and elimination of inert nitrogen, materials with high melting points could be economically smelted. When using higher temperatures in the furnace, care must be taken to ensure that the lining temperatures are within the "specified limits."

With oxygen-enrichment, the slag temperature increases, decreasing its viscosity. The copper particles entrained in the slag settle out much easier, thereby diminishing the copper losses in the slag. Linde[62] found that the copper losses were decreased by 15 to 23 percent with oxygen-enrichment. With the oxygen lancing of bath, Beals et al[63] report a vigorous agitation of the bath and the temperatures of the matte and slag equalized thereby promoting slag cleaning action. Due to this agitation, the fine copper prills in the slag agglomerate and form large copper particles which settle out of the slag in the subsequent quiescent settling zone of the furnace. Higher temperature slag, however, causes greater oxidation of the copper which tends to counterbalance the above effect.[64]

Kupryakov[65] reports that as oxygen concentration in the combustion air increases, the gas velocity through the furnace decreases resulting in a decrease in the dust content in the flue gases. As oxygen content increases above 30 percent, the dust concentration of waste gases starts increasing. This increase is probably due to increase in the mean furnace temperatures and larger duration of the charge feeding operations. Higher temperatures and longer charging periods tend to loosen the charge, increasing the amount of dust entrained with the waste gases.

With oxygen-enrichment, the quantity of the gas per ton of smelting capacity decreases. This results in a lower capital and operating cost of flue gas handling systems per ton of smelting.

As oxygen concentration in the combustion air increases, the SO_2 concentration of the flue gas increases. This increase in SO_2 concentration is due to more charge melted resulting in more sulfur oxidized, higher temperature causing more sulfur to be oxidized, and lower volume of gases through the furnace. With the increase of oxygen concentration beyond 30 percent, the gas volume through the furnace can tend to increase due to false air infiltration through the charging hopper as a consequence of more frequent charging, slag-tapping holes, etc. The result can be that the rate of increase in SO_2 concentration in the flue gas can start to decrease. This effect is, of course, site specific.

3.9.8 REFRACTORY WEAR WITH OXYGEN USAGE

From the literature, it is seen that one of the main controlling factors in the application of oxygen in the reverberatory furnace is the furnace refractory temperature. The roof temperature should not exceed the maximum of the allowable operating range. The experiences on refractory wear with oxygen usage in the reverberatory furnace are given herein. To some extent, the method of oxygen introduction to the furnace dictates the increase in the roof temperature. For example, when oxygen-fuel burners are used (Figure 3-3b) they can release the heat close to the charge, and the roof temperature is not significantly increased. When undershooting the flames with oxygen (Figure 3-3d), high temperatures are created in the vicinity of the charge, but the furnace roof tends to be protected by the flame itself. For these reasons, the aforementioned methods of oxygen-enrichment not only give high thermal efficiency, but also minimize roof wear problem. Oxygen-enrichment of primary air (Figure 3-3e) is very easy to control, but resluts in lower thermal efficiencies than the above two methods of oxygen-enrichment and also increases the roof temperatures.

Saddington et al [66] report that their preliminary investigations indicate that the refractory cost per ton of output in a reverberatory furnace should not increase when oxygen is introduced. By introducing the oxygen below the fuel nozzles, the hottest zone of the flame was found to be at the bottom next to the bath. They demonstrated this by a series of measurements of flame temperatures on two identical reverberatory furnaces, one of which was using oxygen for enrichment. Figure 3-7 shows the temperature variation along the length of the two furnaces taken 4 feet below the top of the furnace roofs. As shown in the figure, when the flame was undershot witn oxygen, the temperature in the vicinity of the furnace roof did not increase significantly.

Table 3-7 gives the measured furnace temperatures at various heights above the slag line at 15 and 25 feet from the burners when oxygen is used in the furnace. As shown in the table, the highest temperatures are produced at about 2 feet above the slag line.

Kupryakov et al [67] report that in examining the operation of the reverberatory furnace with oxygen-enriched blasts, particular attention was given to the condition and the wear of the furnace roof. Under normal operation without oxygen-enrichment, the service life of the reverberatory furnace roof was 26 months. During February 1966, the furnace was given a general overhaul, and the roof was made of 460 mm chrome-magnesite bricks. The roof was the sprung-arch type not generally used in todays designs. With the furnace operating on air blast and using a heat load of 50×10^6 to 70×10^6 Kcal/hr, the roof wear in the highest temperature region after 1 year of operation was 62 mm or 0.17 mm/24 hours. During the period between March 3 and July 21 1967, the roof wear in reverberatory furnace operating on cold blasts (with no preheated air for combustion) dropped to 16-17 mm or to 0.12 mm/24 hours.

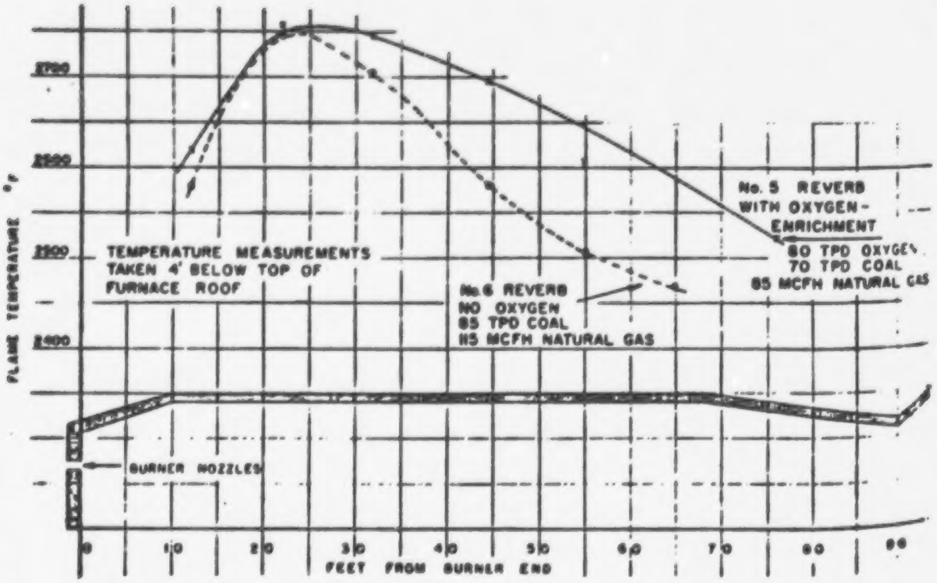


Figure 3-7. Reverberatory Furnace Temperatures in the Vicinity of the Furnace Roofs With and Without Oxygen-Enrichment at INCO Smelter

Table 3-7. MEASURED FURNACE TEMEPRATURES PRODUCED BY OXYGEN-ENRICHED AIR AT INCO SMELTER

Height Above Slag Line (in)	15 ft. From Burners (°F)	30 ft. From Burners (°F)
68	2,620	2,740
36	2,850	2,850
24	3,910	2,890
12	2,895	2,865
9	2,755	-----
6	2,515	-----

During the first test period, the furnace operated on a blast enriched with 25 percent oxygen, the latter being fed through the tuyeres and the air duct. During this period, the wear of the furnace roof reached 5 mm (0.17 mm/24 hours). So a slight change in the roof thickness made it impossible to determine the effect of oxygen concentration in the blast on the roof wear.

The maximum rate of wear was found during the frequent changes in the technological operating conditions of the furnace. Thus, during the period between August 21 and September 21, the reverberatory furnace operated for 7 days on blasts containing 35 percent oxygen fed through tuyeres and 5 days on blasts containing 30 percent oxygen. The furnace operated for 2 days on blasts containing 30 percent oxygen fed through the air duct. For the remaining period of time, the furnace operated on an air blast with fuel consumptions of 6,000, 8,000, 9,000 and 10,000 m^3/hour. During the entire test period, roof wear reached 7 mm or 0.23 mm/24 hours.

When reverberatory smelting is performed on blast containing 35 and 40 percent oxygen, fed through tuyeres and the air duct, furnace wear reached a rate of 0.18 mm/24 hours.

During the entire test period, the average wear of the furnace roof reached a rate of 0.2 mm/24 hours. Taking into account the measurement accuracy and the frequent changes in the technological operating conditions on the furnace, the wear of the furnace roof during reverberatory furnace operation on oxygen-enriched blasts did not differ markedly from wear when operating with conventional air blasts.[68]

Itakura et al [69] report that using oxygen-fuel burners in the reverberatory furnace did not increase the lining wear. This is probably due to the heat being released close to the charge rather than the lining.

Wrampe and Nollman [70] report during their work on oxygen-enrichment at reverberatory furnaces at various U.S. smelters, that the overall refractory temperatures increased by approximately 0.5°F per mscfm of oxygen. During their tests, excessive roof temperatures did not become a problem until production increases exceeded 50 percent.

The Caletones smelter experience [71, 72] indicated that it was necessary to use a bottom ventilation system but that roof refractory wear was in the range of 10 percent over a 6 months operating period. Maximum temperatures were no higher than "normal" operation and more uniform temperature distribution was obtained.

3.9.9 CONCLUSION

The theoretical as well as experimental and operational results on oxygen-enrichment in a reverberatory furnace indicate the feasibility of using oxygen to increase SO_2 concentration in the flue gas. The controlling factors in the application of oxygen to a reverberatory furnace are, feed characteristics, furnace refractory and slag temperatures, and the auxiliary material handling capabilities. According to Linde's [73] experience, excessive roof temperatures do not become a problem until production increases exceeding 50 percent are desired. Kuprayakev et al [47] Itakura et al [75] and Saddington et al [76] also report the lining wear to be not very different with or without oxygen-enrichment. With an increase in material temperatures, slag handling becomes difficult with excessive fluidity, but this, according to Wrampe et al [77] can be easily corrected by flux adjustment in the future.

From the economic point of view, oxygen-enrichment should be used to increase the smelting rate. When no production increase is desired, the quantity of sulfur available for oxidation from the feed remains constant. The volume flow of gas through the furnace would decrease with oxygen addition, and some additional sulfur oxidized from the charge and the SO_2 concentration in the flue gas would be increased. In the case of increased production, not only is the specific fuel consumption decreased, but the concentration of SO_2 is further increased in the flue gases. Figure 3-8 shows the relationship between fuel, smelting, flue gas, and oxygen rates and SO_2 concentration. While the quantitative values may vary from case to case, the relative relationships are indicated.

3.10 PREDRYING WET CHARGE

Concentrates, as received at the smelter, generally contain 8 to 12 percent moisture, although this could vary widely depending on the location and season. In the green charge reverberatory furnace not only must this substantial amount of water be evaporated, but the resulting water vapor must be heated to the temperature of the smelting furnace offgases (2,350°F). The water vapor adds to the volume of hot gases that must be treated and thus reduces the capacity of the smelting furnace.

Concentrate drying prior to smelting still requires energy for evaporation of water, but the water vapor may leave the dryer at temperatures as low as 180°F so that considerably less fuel is requirement for drying than for handling the same amount of moisture in the wet-charge reverberatory furnace. An additional advantage is that dry concentrates frequently retain a small amount of sensible heat from the drying operation. This sensible heat would account for a small reduction in smelting furnace fuel requirements, as well as reducing dilution nitrogen producing a small net increase in SO_2 concentration.

A further advantage to drying the charge material is the added capability for furnace sealing to minimize infiltration air. By limiting moisture the possibility of destructive water vapor explosions or pressure surges is minimized.

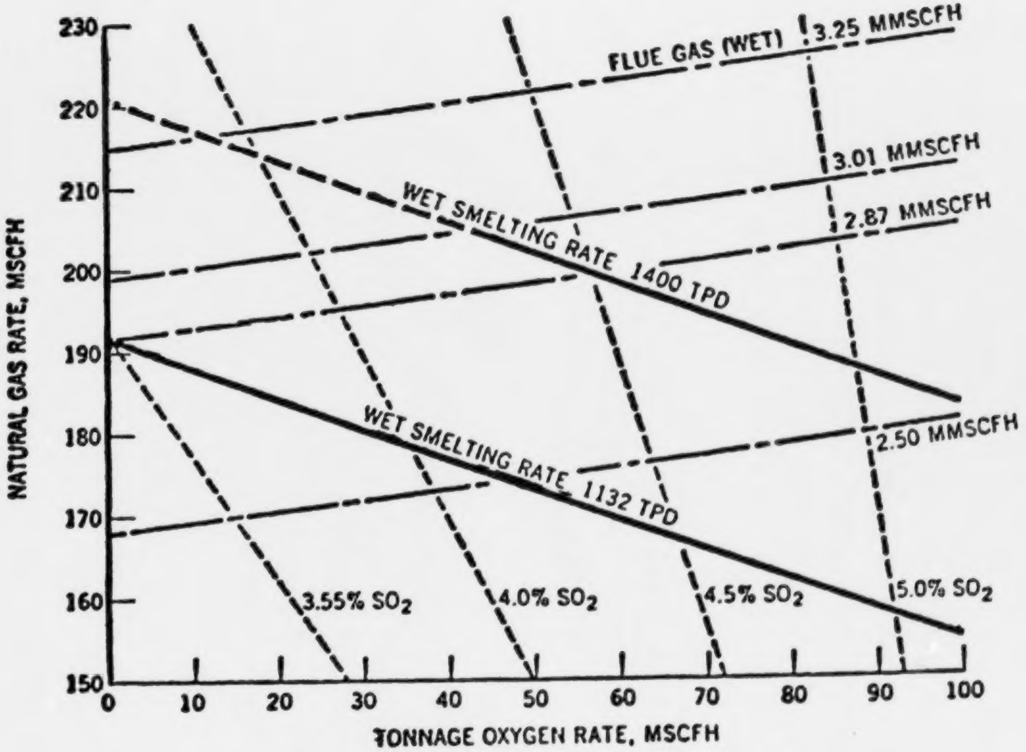


Figure 3-8. Reverberatory Production and Flue Gas Dependence Upon Tonnage Oxygen and Fuel[77]

3.11 CONTINUOUS FURNACE CHARGING

Most U.S. smelters use Wagstaff guns for calcine reverberatory furnace charging (Section 2.0) resulting in fluctuations in SO_2 concentration in the offgas. As soon as the feed material enters the bath the greatest generation of SO_2 is encountered, followed by a gradual reduction until the next charge point.

With smaller quantities charged at more frequent intervals, approaching continuous feed, a more steady-state SO_2 concentration versus time can be achieved and peak values will be minimized. This characteristic will minimize the size and cost of subsequent SO_2 control equipment since one of the major design criteria is peak SO_2.

The Copper Cliff Smelter of INCO Metals Ltd., is side wall-charged on a continuous basis. It is further discussed in Appendix C.

3.12 ELIMINATION OF THE REVERBERATORY FURNACE

The extensive consideration and discussions being held throughout the world on modified copper smelting processes such as the Noranda, the Outokumpu flash smelting, the Mitsubishi continuous smelting processes, various chemical processes, and the use of electric furnaces rather than the combustible fuel reverberatory furnace all seem to indicate that great changes are in progress for the processing portion of the copper industry. Despite the many advantages and the "forgiving" nature of the reverberatory furnace, the high energy consumption of the green feed furnace will certainly subject it to continuous review in the future comparing it with the new processes currently being developed. Calcine charge furnace processes may be energy competitive.[79]

At the very least, the new processes tend to produce smaller quantities of offgases per ton of produced copper and generally produce higher concentrations of SO_2. This obviously makes SO_2

control more cost-effective and production easier which will no doubt be a prime consideration for future decisions.

It can certainly be said that there is now and will be more serious thought given to elimination of the reverberatory furnace during the next few years. However, we hasten to add that there are many people in the industry who feel very strongly that the reverberatory furnace is a reliable, easy to operate device with many characteristics that, from a smelting standpoint, introduce great flexibility and operational advantages.

3.13 CONVERTER SCHEDULING AND HOODING

The availability of a strong SO_2 stream can provide some flexibility in processing streams by blending, since the converter can produce a gas stream containing over 10 percent SO_2. When it is picked up by conventional hooding with 100 percent dilution air, this will reduce to over 5 percent SO_2 during the slag blow. (See Appendix H for calculations.) During the copper blow, SO_2 gases with a concentration as high as 28 percent (which would be reduced to 14 percent with dilution air inside the pickup hood) are produced.

A typical converter sequence including slag blowing, copper blowing, and charge times can take between 11 and 12 hours per charge. Slag blow will be approximately 6 hours, copper blow approximately 2 hours, and offtime, which includes charging and pouring, approximately 3 hours.

The SO_2 content of the off-gas for a single converter is shown as a function of time in Figure H-1 using the assumptions discussed in Appendix H. Based on the calculations, five converters would be necessary to have one converter in the copper blow at all times. However, this condition is not, of course, attainable with fewer than five converters. Figure H-2 shows the scheduling for three converters which will allow one converter producing high concentration SO_2 at all times (either copper or slag blows). Figure H-1 also shows the flow rate fluctuations during operation.

Thus, scheduling of converters can provide a more steady stream of SO_2 to the acid plant and, with three converters or more, maintain a high concentration of SO_2.

Converter hooding systems are extremely critical in terms of maintaining high SO_2 concentrations in the offgas going to the acid plant. It is difficult to obtain and maintain a close fitting hood because of several factors including out of roundness of the converter, buildup of molten-solidified material on the converter mouth, and occasional crane damage. Chain curtains or sheet metal tabs have been used to minimize the effective gap between the bottom of the converter hood and the converter mouth. These approaches tend to compensate for the unevenness of the matching surface and minimize dilution air intake.

3.14 BLENDING

Blending of rich SO_2 streams with lean SO_2 streams to provide proper concentration for direct processing in a sulfuric acid plant has been conventional practice in the industry with fluid-bed roasters and converter offgases. Reverberatory furnace offgases are blended with continuous smelting process offgases at the Naoshima smelter in Japan and sent directly to a sulfuric plant (Appendix G). If sufficiently high SO_2 concentrations in other offgas streams are avilable to match the acid plant requirements, then blending of reverberatory furnace offgas can be accomplished. A study of some of the many possible plant emission desulfurization scenarios for new smelters is presented in Section 6.0.

With current industry reverberatory furnace practice resulting in average SO_2 concentration from green charge furnaces of 1.0 to 1.5 percent, calcine charge reverberatory furnaces 0.5 to 1.0 percent, and their large gas volume flow rate (over 100,000 scfm), it is expected that this approach would generally be marginal. With increased reverberatory furnaces SO_2 concentration, the use of fluid-bed roasters and programmed converter operation to minimize SO_2 fluctuations, blending is a potential approach to producing a gas for direct acid plant processing with current operational smelters. The addition of SO_2 concentration systems as discussed in Section 5.0 would also allow the use of the blending technique.

SECTION 4

DIRECT ACID PLANT PROCESSING

4.1 INTRODUCTION

Conventional single contact sulfuric acid plants will operate autothermally in a minimum range of 3.5 to 4.0 percent input SO_2 concentration, and conventional double contact sulfuric acid plants will operate autothermally in the minimum range of 4.0 to 5.5 percent SO_2 concentration. This operation occurs because a minimum temperature (approximately 800°F) is required to cause "ignition" in the catalyst bed to promote the oxidation of SO_2 to SO_3. The reaction proceeds exothermally in the catalytic converter. The heat generated raises the temperature of the gas to the point where the efficiency of the reaction tends to decrease (approximately 1,100°F). The gases are then brought out of the catalytic converter and enter heat exchangers where the heat is removed so that the gases can enter a second layer of catalyst to continue the reaction. The heat removed is transferred into the incoming gas to provide the thermal energy necessary to reach the required inlet temperature of approximately 800°F. When the SO_2 concentration is below the minimum values (e.g., double contact 4.5 to 5.5 percent), there is not sufficient heat available to raise the gases to the ignition temperature.

A second problem also occurs in the operation of the conventional sulfuric acid plant using low concentrations of SO_2. If the gas containing SO_2 is not sufficiently dried, it will carry moisture that will dilute the product acid. The lower the SO_2 concentration in the gas, the lower will be available concentrated acid that can be used to absorb incoming moisture. The conventional technique for removing moisture is to first preprocess by reducing the temperature of the incoming gas with water sprays. This reduces any excess moisture to that at saturation conditions. The gases are then passed through a drying tower where concentrated acid is used to absorb the remaining moisture. The amount of concentrated acid available must be sufficient to not be diluted below the product concentration requirement. Or conversly the temperature of the cooled gas must be low enough so that sufficient moisture has been condensed to maintain the plant water balance. If spray water temperatures are not low enough, then concentrated (93 or 98 percent) acid cannot be produced.

Thus, the two basic reasons why low concentration gases cannot be processed directly in a conventional sulfuric acid plant are (1) insufficient heat is generated to maintain ignition temperature in the catalyst bed, and (2) system water exceeds the minimum content required to produce concentrated acid. It is possible to resolve these problems by providing additional thermal energy and refrigeration.

The existence of a basically different acid making approach called the chamber process should be noted here even though in current commercial practice this process is considered obsolete. The reason the contact process is the commercial process used today is because it can produce up to 100 percent concentration of sulfuric acid as well as oleum. The chamber process can only produce concentrations up to 70 to 75 percent. The reason for noting this process is that it can use SO_2 concentrations as low as 0.5 percent which means that reverberatory furnace offgases could be fed directly to this type of plant. If the product acid were to be used for applications where lower concentration acid is needed (e.g., fertilizer production or leaching) then this design should be considered. Obviously, the lower concentration acid would need to be used very close to the production point to be economically feasible because of shipping costs.

A general discussion on metallurgical contact acid plant design, a description of work performed at the Onahama Smelter where an acid plant was actually operated on low concentration copper reverberatory furnace offgases, and several potential techniques for solving these problems, are described in this section.

4.2 METALLURGICAL ACID PLANT DESIGN

There is a distinct difference between the requirements for a conventional acid plant using SO_2 generated by burning sulfur when compared to a plant operating on offgases from a metallurgical process. The major difference is in terms of the objective in the operation of the plant. The metallurgical gas plant has in most cases been installed primarily for pollution control purposes and only secondarily to produce sulfuric acid. As a result of this the metallurgical processes tend to control the operation of the acid plant.

The sulfuric acid plant by its nature is a constant process device. It requires a steady state feed and temperature condition throughout the process. When used in conjunction with a metallurgical plant it can be operated only when the feed gas is available. While auxiliary SO_2 feed systems can be applied, this has not been current practice in the United States' metallurgical plants.

Thus the metallurgical acid plant is forced to operate with continuous starts and stops resulting in temperature changes from the high operating range to ambient. This causes the gas condition within the plant to pass through saturation temperature with subsequent acid condensation in various critical areas of the system. Resulting corrosion can be extensive if proper materials are not used. Startup can take a relatively long period of time. It may take as long as 8 hours to reach steady state temperature conditions from a cold start. On the other hand, if the plant is designed with suitable insulation, temperatures can be maintained for as much as 6 to 8 hours and still have sufficient heat available for a rapid startup.

Thus, the design of a metallurgical sulfuric acid plant must take into account the specific problems related to this application. Proper process selection, engineering design, plant construction, startup, operation and maintenance are all important to the successful and long-term operation of a metallurgical sulfuric acid plant. It has been demonstrated at some smelters using a double contact acid plant that 200 ppm SO_2 emission level can be consistently accomplished. In addition, on stream factors of well over 99 percent can also be accomplished with proper application of the above factors.

One example is the Amax molybdenum smelter at Fort Madison, Iowa where only 9 hours of down time (exclusive of annual maintenance) have been encountered in over 3 years of operation and emissions average 200 ppm. The addition of supplemental sulfur dioxide when the smelter is not producing a suitable feed stream (by burning sulfur) and the use of additional catalyst are two two approaches used at this plant that can improve operation.

The use of a double contact sulfuric acid plant is not necessarily always the most advantageous design approach. The reason for this is that the single contact design can operate autothermally at an SO_2 concentration of approximately 3.5 percent whereas the minimum concentration for the double contact is 4.5 percent. When the blending technique is considered (see Section 6.0) there are some conditions where only a lower blended stream SO_2 concentration can be produced which can match the minimum for a single contact plant but not high enough for a double contact plant. Therefore, it is necessary to evaluate the impact of the alternative control techniques upon overall reduction of SO_2 emissions from the smelter based upon site-specific conditions, especially in the case of retrofitting.

4.3 ONAHAMA SMELTER EXPERIENCE

The Onahama Smelting and Refining Company, located at Onahama Harbor about 90 miles north of Tokyo, incorporated into their smelter a reverberatory furnace offgas sulfuric acid plant in 1971 and successfully operated this system to 1973. This sulfuric acid plant was reconstructed from an existing single contact plant which was no longer being used. The SO_2 gas liberated from the green charge feed reverberatory furnace had been passed through two parallel boilers, a hot Cottrell electrostatic precipitator, and then vented to the atmosphere through a 560 ft stack. It was decided to build a new double contact sulfuric acid plant to treat the existing copper converter offgases. As a result of this installation, the existing single contact acid plant, which had previously served to manufacture sulfuric acid from this gas, was no longer needed.

The green charge material fed into the reverberatory furnace varied from 24 to 34 percent sulfur, averaging 33 percent. The low strength reverberatory offgases contained approximately 1.5 percent SO_2. It was found that due to the cost of utilities, it would be more desirable to operate the sulfuric acid plant at higher gas strengths.[80] At times, the Onahama Plant operated with 1 to 1.5 percent SO_2 gas; however, by using oxygen and fuel burners and by closing considerable leakage of secondary air to the system, the gas strength entering the sulfuric acid plant could be raised to approximately 2.5 percent SO_2. The modified reverberatory furnace sulfuric acid plant handled approximately 90,000 m^3 per hour (approximately 53,000 scfm) of purified reverberatory gas

The remodeled single contact sulfuric acid plant acheived efficiencies of 96 percent conversion of SO_2 to SO_3 even at low concentrations of 1.5 percent SO_2 fed into the sulfuric acid plant converter. This sulfuric acid plant could produce product acid strength of 93 to 94 percent H_2SO_4.

A simplified flowsheet of the plant is shown in Figure 4-1.[81] The reverberatory furnace gas, after passing through the waste heat boilers, passes to a hot Cottrell precipitator. The gas is then carried to a washing tower and two series of gas coolers. The first is cooled by sea water and the second by a chilled water refrigeration unit. The gas leaving the gas coolers (condensers) then passes to a wet Cottrell precipitator and then into a sulfuric acid drying tower. After the gas has been dried of water in the drying towers, it is passed to the preheater heat exchanger which supplements the heat required to preheat the gas flowing to the sulfuric acid plant converter. The gas, after passing through the converter, is then returned to the heat exchangers. It then passes through the absorption tower and through a limestone scrubber and wet Cottrell precipitator before being vented back to the atmosphere.

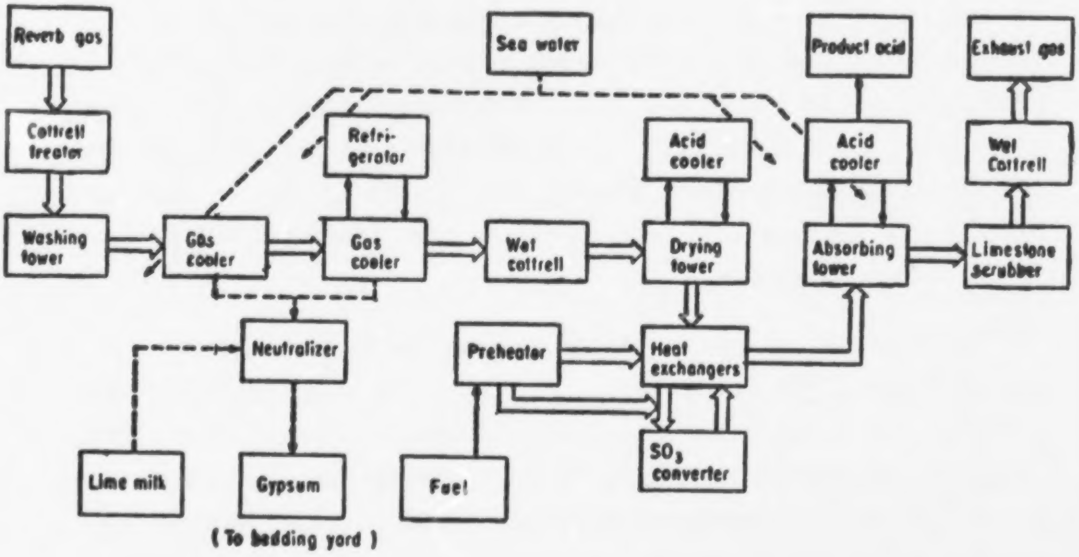

Reverb gas
Cottrell treater
Washing tower
Gas cooler
Refri-gerator
Gas cooler
Sea water
Wet cottrell
Acid cooler
Drying tower
Product acid
Acid cooler
Absorbing tower
Exhaust gas
Wet Cottrell
Limestone scrubber
Neutralizer
Lime milk
Gypsum
(To bedding yard)
Preheater
Fuel
Heat exchangers
SO_3 converter

Figure 4-1. Flowsheet of Remodeled Acid Plant

Two problems existed in the Onahama Plant which are responsible for high operating cost. One is the power required to refrigerate the chilled water which condenses excess moisture in the gas (required to achieve water balance) to produce concentrated sulfuric acid. The other problem is the consumption of fuel used in preheating the gas required because at the low (not autothermal) SO_2 concentration. Not enough exothermic energy in the SO_2 to SO_3 conversion is generated to preheat the gas flowing to the converter to "ignition" temperature.

4.4 REDUCED ENERGY SYSTEM

Since the Onahama approach to direct processing of reverberatory furnace offgas under full-scale conditions for SO_2 control had been demonstrated at the cost of extra energy, this technique was reviewed to determine if the process could be made more efficient and economical.

A simplified flowsheet showing an Onahama-type acid plant applied to a copper smelter to process reverberatory furnace offgases is shown in Figure 4-2. This flowsheet indicates the fluid flow circuits and equipment. It is not significantly different from the system used at Onahama; however, it is included as the base-case to show the modifications made to obtain the subsequent improved system discussed herein.

An improved process developed recently by the author is described hereafter and includes flowsheets and pilot plant for the sulfuric acid plant known as the Browder process (Figure 4-3). This reverberatory gas sulfuric acid plant is similar to the Onahama Plant and similar to a conventional standard single contact plant in the gas flow after the drying tower. However, certain modifications have been made in the process which greatly improve the operation while decreasing the utility consumption for the reverberatory gas sulfuric acid plant process.

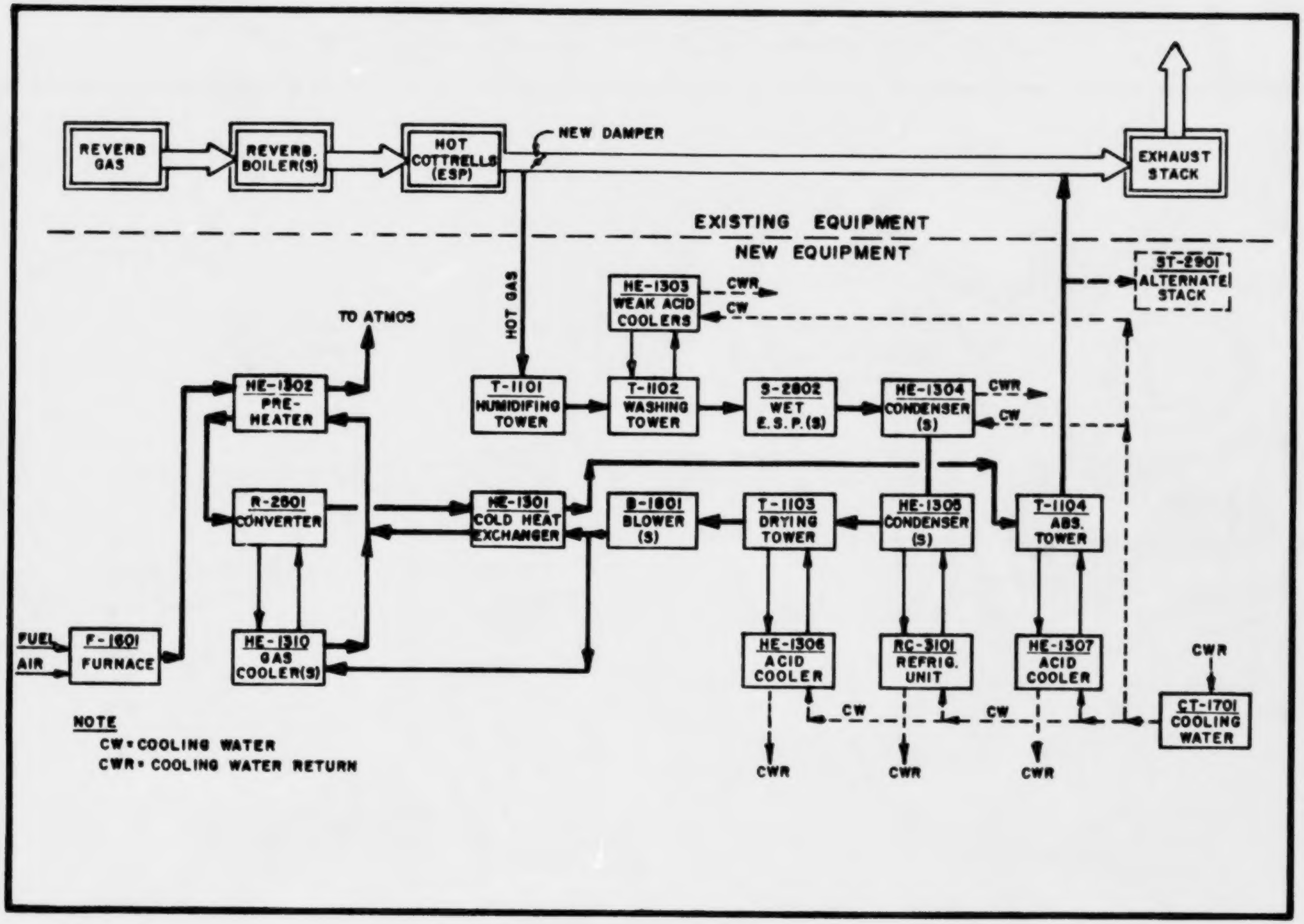

REVERB GAS
REVERB. BOILER(S)
HOT COTTRELLS (ESP)
NEW DAMPER
EXHAUST STACK
EXISTING EQUIPMENT
NEW EQUIPMENT
HOT GAS
ST-2901 ALTERNATE STACK
HE-1303 WEAK ACID COOLERS
CWR
CW
TO ATMOS
HE-1302 PRE-HEATER
T-1101 HUMIDIFING TOWER
T-1102 WASHING TOWER
S-2802 WET E.S.P.(S)
HE-1304 CONDENSER (S)
CWR
CW
R-2601 CONVERTER
HE-1301 COLD HEAT EXCHANGER
B-1801 BLOWER (S)
T-1103 DRYING TOWER
HE-1305 CONDENSER (S)
T-1104 ABS. TOWER
FUEL
AIR
F-1601 FURNACE
HE-1310 GAS COOLER(S)
HE-1306 ACID COOLER
RC-3101 REFRIG. UNIT
HE-1307 ACID COOLER
CWR
CT-1701 COOLING WATER
CW
CW
CWR
CWR
CWR
NOTE
CW = COOLING WATER
CWR = COOLING WATER RETURN

Figure 4-2. Simplified Flowsheet of Reverberatory Gas Sulfuric Acid Plant - Onahama Process - Case I

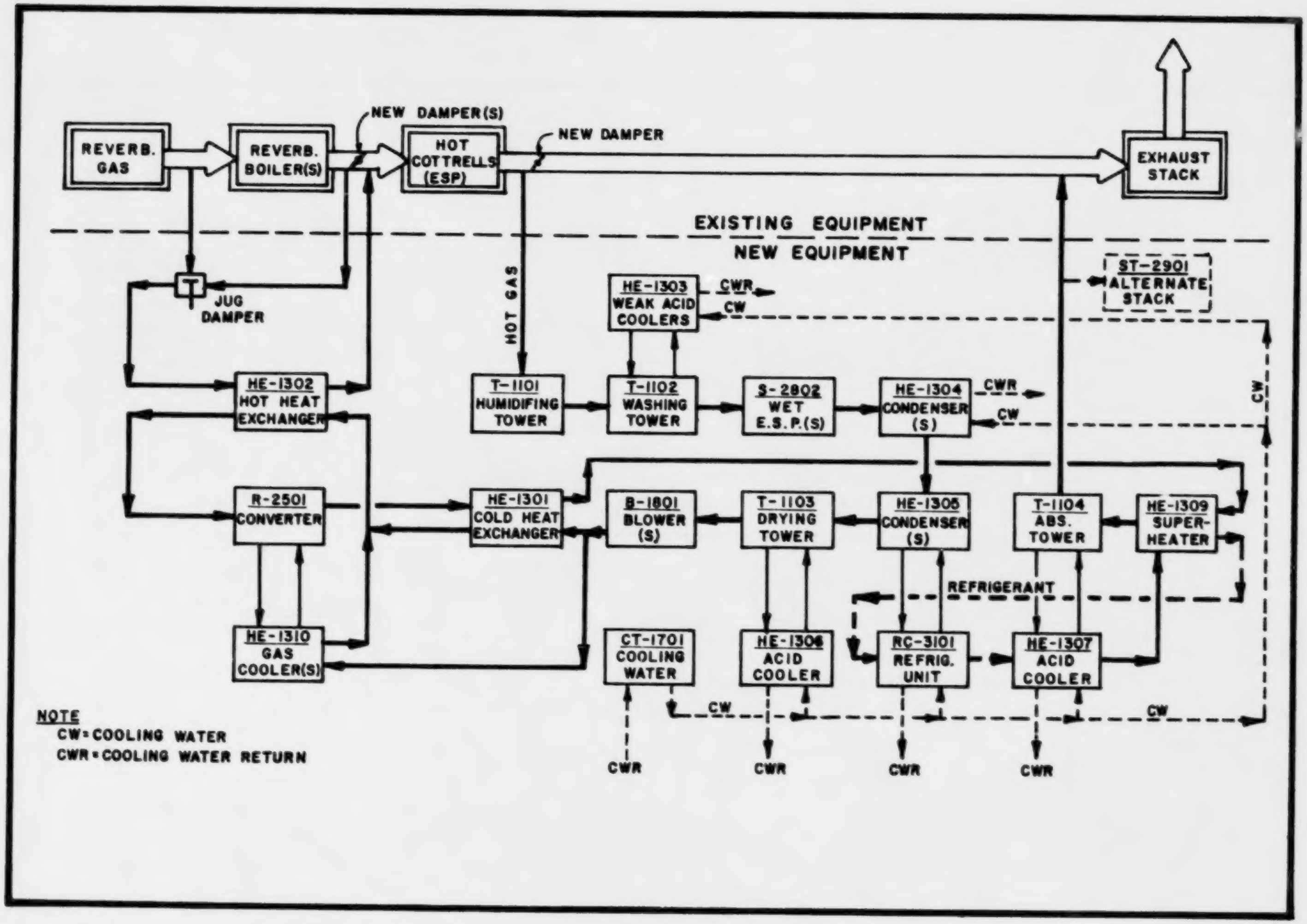

NEW DAMPER(S)
NEW DAMPER
REVERB. GAS
REVERB. BOILER(S)
HOT COTTRELLS (ESP)
EXHAUST STACK
EXISTING EQUIPMENT
NEW EQUIPMENT
ST-2901 ALTERNATE STACK
JUG DAMPER
HOT GAS
HE-1303 WEAK ACID COOLERS
CWR
CW
HE-1302 HOT HEAT EXCHANGER
T-1101 HUMIDIFING TOWER
T-1102 WASHING TOWER
S-2802 WET E.S.P.(S)
HE-1304 CONDENSER (S)
CWR
CW
CW
R-2501 CONVERTER
HE-1301 COLD HEAT EXCHANGER
B-1801 BLOWER (S)
T-1103 DRYING TOWER
HE-1305 CONDENSER (S)
T-1104 ABS. TOWER
HE-1309 SUPER-HEATER
REFRIGERANT
HE-1310 GAS COOLER(S)
CT-1701 COOLING WATER
HE-1306 ACID COOLER
RC-3101 REFRIG. UNIT
HE-1307 ACID COOLER
CW
CW
CWR
CWR
CWR
CWR
NOTE
CW=COOLING WATER
CWR=COOLING WATER RETURN

Figure 4-3. Simplified Flowsheet of Reverberatory Gas Sulfuric Acid Plant - Browder Process - Case II

The proposed system is essentially a single contact sulfuric acid plant which uses all components with proven technology. The main difference is that the individual proven components are rearranged into a unique system whereby the preheater fuel consumption in a standard weak gas operating plant is reduced to zero by using approximately 8 percent of available waste heat boiler energy. The externally supplied refrigeration energy required in a low SO_2 concentration gas single contact plant to achieve water balance is also reduced to zero. This occurs by using excess heat generated in the acid plant, which normally is passed to the atmosphere by cooling tower. Detailed engineering analysis of a typical system is included in Appendix K.

The new process overcomes the difficulties encountered with high fuel consumption in the Onahama process. This is achieved by recovering heat from some of the reverberatory furnace hot gas instead of burning fuel in the preheater to preheat the gases flowing to the converter as in the Onahama process. The other features of this process include the elimination of the electrical energy required for refrigeration and water chillers. The heat normally dissipated by cooling water in the sulfuric acid coolers for the absorption tower is recovered as useful work.

The process starts with a hot gas which can be 600° to 650°C (1,100° to 1,200°F). This temperature of gas is achieved by mixing reverberatory gas leaving the furnace upstream of the waste heat boilers with boiler exit gas in the appropriate amount to give the temperature range mentioned. This gas is then conveyed through a brick-lined insulated duct into a top vestibule of a vertically mounted shell and tube heat exchanger. The hot gas passing through the large tubes then goes into a knockout section and is returned to the main gas stream of the reverberatory boiler outlet. This remaining gas which has been first used for preheating a hot exchanger then passes to the hot Cottrell precipitators. The hot exhanger used takes the place of the fuel-fired preheater used in the Onahama process. This does, however, reduce the production of steam in the waste heat boilers by approximately 8 percent.

The hot heat exchanger is essentially a down flow shell and tube heat exchanger similar to a fire tube waste heat boiler. The location of the hot heat exchanger in the system would be similar to the location of the waste heat boiler functioning in a reverberatory furnace gas smelting plant. Reverberatory furnace boilers have been used for many years to cool the reverberatory gas passing through to hot Cottrell precipitators and thereby recover the energy in the form of steam. The normal reverberatory boilers are essentially heat exchangers recovering energy in the form of steam from hot gases passing through the boiler. However, most of the reverberatory boilers are of a water tube-type.

The hot heat exchanger used serves the same purpose as the reverberatory furnace boilers in the Onahama process. For many years, the metallurgical industry has attempted to recover heat in gas to gas heat exchangers without much success. The recovery of heat in gas to gas exchangers has been attempted by passing hot gas across the tube bundle, through banks of tubes, or through finned tubes. This design has been completely unsatisfactory because the gas, which contains dust, has allowed the dust to impinge and collect upon the heat transfer surface (tubes), thereby easily fouling the tubes and bridging across the tubes to completely block the heat exchanger to any further gas flow.

The design of the hot heat exchanger handling reverberatory gas uses a different concept. This heat exchanger shown in Figure 4-4 receives hot metallurgical gas in a top refractory-lined vestibule and the gas flows through the tubes similar to gas flow in a fire tube waste heat boiler. The main difference between this heat exchanger and a fire tube waste heat boiler is that most fire tube waste heat boilers are mounted in a horizontal position. The design of this heat exchanger will not allow any dust to impinge directly on the tubes since there is no cross flow of dust. The gas, after

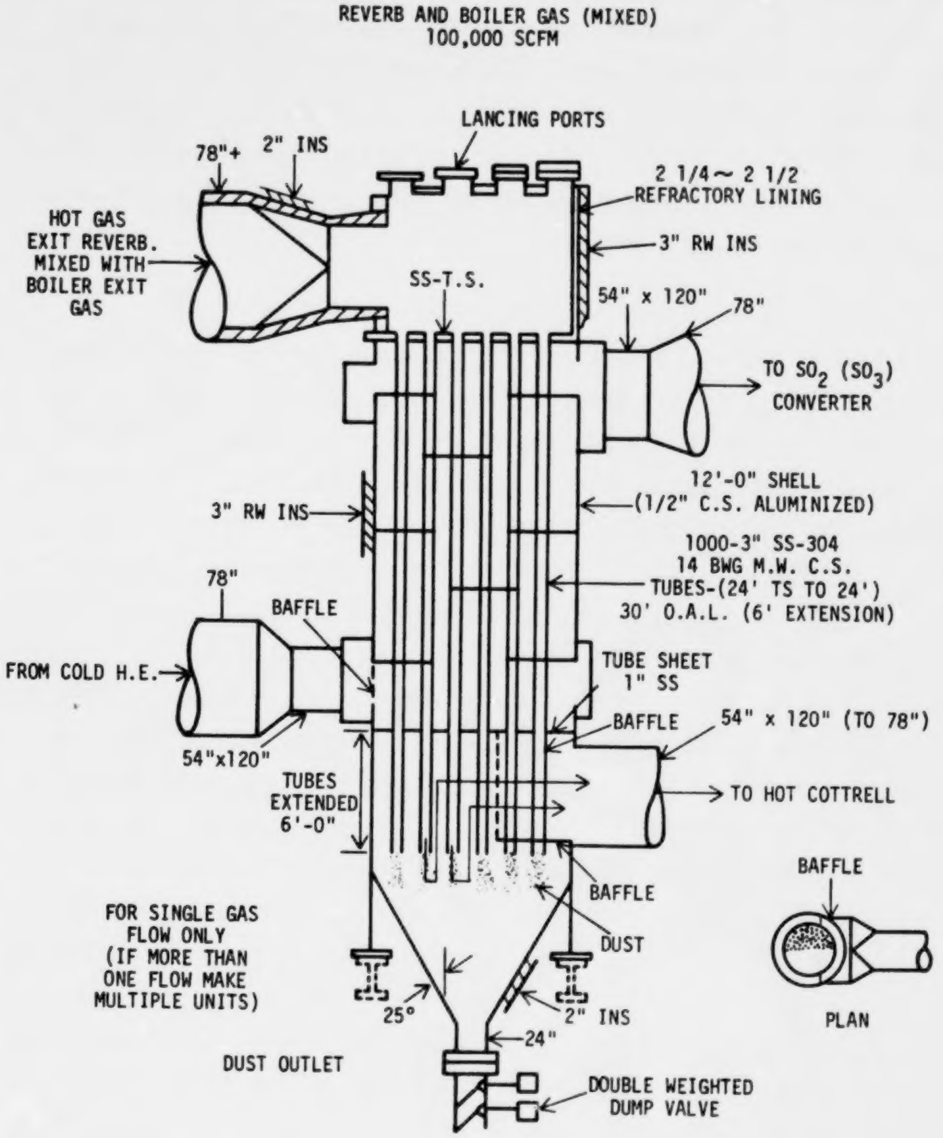

REVERB AND BOILER GAS (MIXED)
100,000 SCFM
LANCING PORTS
78"+
2" INS
2 1/4 ~ 2 1/2
REFRACTORY LINING
HOT GAS EXIT REVERB. MIXED WITH BOILER EXIT GAS
3" RW INS
SS-T.S.
54" x 120"
78"
TO SO_2 (SO_3) CONVERTER
12'-0" SHELL
(1/2" C.S. ALUMINIZED)
3" RW INS
1000-3" SS-304
14 BWG M.W. C.S.
TUBES-(24' TS TO 24')
30' O.A.L. (6' EXTENSION)
78"
BAFFLE
FROM COLD H.E.
TUBE SHEET
1" SS
BAFFLE
54" x 120" (TO 78")
54"x120"
TUBES EXTENDED 6'-0"
TO HOT COTTRELL
BAFFLE
BAFFLE
FOR SINGLE GAS FLOW ONLY (IF MORE THAN ONE FLOW MAKE MULTIPLE UNITS)
DUST
25°
2" INS
24"
PLAN
DUST OUTLET
DOUBLE WEIGHTED DUMP VALVE

Figure 4-4. Hot Heat Exchanger

entering the top vestibule, flows through 3-in diameter tubes. The selection of 3-in tubes was made to prevent fouling or bridging which occurs in smaller tubes. The triangular pitch of the tube arrangement is such that all tubes are placed on a 4-in triangular pitch. Therefore, only a 1-in space exists between adjacent tubes. The top tube sheet, therefore, has no large areas in which dust can settle out on the tube sheet.

Since a small amount of minor dust may adhere to the inner walls of the tubes, components are included in this hot gas heat exchanger design to allow for maintenance and cleaning by lancing of the tubes from above the top vestibule. It is suggested that the proper lancing media would be dry-compressed weak SO_3 gas leaving the sulfuric acid plant drying tower blower. The analysis of this gas is essentially the same as the gas flowing through the tubes of this hot heat exchanger. A self-cleaning feature of this hot heat exchanger is a knockout section in the lower vestibule. This knockout section is incorporated by extending the 3-in heat exchanger tubes below the tube sheet into the lower vestibule by approximately 6 feet. The gas leaving the tubes, therefore, must turn and flow countercurrent to the tubes causing a reversal in gas flow and knockout of any large particles of dust which would normally settle out in the lower vestibule. The lower vestibule has a conical bottom with an angle greater than the angle of repose of the dust thereby allowing any dust leaving the tubes and settling in the vestibule to be removed from the bottom nozzle. Weighted double airlock valves allow the dust to be removed from the system even though it is under vacuum.

This hot heat exchanger also serves as a preheater for starting the entire sulfuric acid plant from a cold state. When it is used as a preheater, gases of approximately 700°C to 760°C (1,300°F to 1,400°F) are then passed through the top vestibule and down through the tubes of the exchanger and vented into the waste heat boiler outlet. A reduced flow of dry air from the sulfuric acid plant main blowers is then passed through the cold heat exchanger and into the shell side of the hot exchanger serving as a preheater. The dry air is thereby preheated to approximately 480°C to 510°C (900°F to 950°F), the required temperature for preheating the catalyst in the converter for startup. This high temperature operation is required for approximately 30 to 48 hours for starting the sulfuric acid plant assuming no residual heat from previous operations.

If pollution regulations require that reverberatory furnace vent gas not be vented to the atmosphere during the startup phase, then the gas which is used for the preheating operation could be discountinued and in its place preheated air of 700°C to 760°C (1,300°F to 1,400°F) used for preheating operation of the acid plant converter. A fuel-fired furnace could be installed with the products of combustion passing into the hot vestibule just as the reverberatory gas was used. After the plant has been started in 30 to 48 hours, this combustion furnace would be discontinued and the mixed gas from the reverberatory having a temperature of 600°C to 650°C (1,100°F to 1,200°F) would then be passed through the hot heat exchanger. The shell side (flow of the gas across the tubes) of this hot heat exchanger would be passing to the converter. There would be no possibility of fouling of this heat exchanger provided it was properly designed and operated.

A hot heat exchanger which has been properly designed would not present any abnormal operations or maintenance provided the proper materials for construction were selected. Therefore, a refractory-lined head, stainless steel tube sheet, and tubes have been selected as the required material of construction for this design. In later sections of this report and Appendix K, the flow scheme and equipment of this plant are described in more detail.

Using a chilled water gas cooler (condenser), essentially the same as used at Onahama, will not consume any power under normal operations. This is not true of the Onahama process. Operating at a gas flow of 170,00 Nm^3/hr (100,000 scfm) entering the sulfuric acid plant converter as the base point, the plant is only slightly less than twice the size of the Onahama plant.

Also, considerably less recovered energy is used than the purchased energy used at Onahama. Besides the energy taken from the reverberatory gases for preheat, a somewhat unique feature is incorporated whereby the energy required for refrigeration is recovered from that normally wasted in the sulfuric acid absorption tower acid coolers. This is accomplished by the addition of a superheater located in the hot gas stream before the absorption tower.

A somewhat similar heat recovery system has been proposed and used in Japan by Ishikawajima - Harima Heavy Industries Company, Ltd. This company has head offices in Tokyo, Japan. The Ishikawajima Heat Recovery Process (Appendix K-2) uses a Rankine cycle heat recovery system. The system used by Ishikawajima starts with a liquid-fed pump, pumping Freon (or another low boiling point fluid) through two sets of heat exchangers in series. The first heat exchanger is a liquid heater and the second heat exchanger is a Freon boiler. Hot sulfuric acid from the absorption tower is cooled by these two heat exchangers in countercurrent flow. The Rankine cycle heat recovery from this Ishikawajima system permits saturated Freon to flow to an expander turbine where the saturated vapor leaving the boiler is expanded. In the turbine, energy is recovered and the vapor is then vented at lower pressure into the condenser. The Freon leaving the condenser goes to a receiving tank and is then recycled and pumped back into the system again. At the present time, Allied Chemical Company is currently operating a pilot plant to recover heat on one or more of their sulfuric acid plants using this type process. The data included in Appendix K is from Allied Chemical Company on energy conservation through the application of a low temperature Rankine cycle using a similar system.

The difference between the Ishikawajima/Allied Chemical Company process and the Browder process is that the Freon is used more efficiently by superheating the saturated vapor leaving the (acid cooler) boiler in the latter process. This is accomplished by passing the saturated vapor from the Freon boiler to a superheater located between the sulfuric acid plant cold heat exchanger and the absorption tower. This superheater greatly increases the temperature of the Freon vapor and also increases the enthalpy, thereby allowing for a higher energy recovery level of the vapor going to the expansion turbine. This improved feature permits three times the power recovery in KW than that used in the Allied Chemical Company Report. In the flow scheme of the Allied application (Appendix K), the Freon is heated from 41°C to 88°C (105°F to 190°F) before passing into the expansion turbine. The enthalpy of the saturated boiler exit Freon is 132 Btu per pound at the saturated vapor temperature of 88°C (190°F). After leaving the expander at 41°C (105°F), the Freon enthalpy is 121 Btu per pound, leaving a differential enthalpy of 11 Btu per pound of Freon for available work recovered in the expander turbine. The Browder process heats the Freon from the saturated condition to a superheated condition of between 140°C and 150°C (280°F and 300°F) which has an enthalpy in excess of 154 Btu per pound of Freon. This, when expanded through the expander turbine, will yield 154 minus 121 or 33 Btu per pound of Freon which is three times the heat recovered in the Allied process and is used for refrigeration.

Water chillers similar to those in the Onahama Refining and Smelting Plant are used. These can be purchased as standard units from refrigeration manufacturers such as York, Carrier, or others. Package water chillers are readily available in the range of 90 to 650 tons of refrigeration. These package units usually are motor-driven; however, they can be purchased without the electric motors or can be purchased with electric motors with shaft extensions or additional turbine expander drives. The flowsheet (Figure 4-4) shows superheated Freon vapor passing through an expansion turbine which operates the water chillers and, thereby, eliminates the electric power used to chill water for the secondary condensers (gas coolers used in the system). It would be suggested that the water chillers still have electric motors which could be used for startup purposes only until the sulfuric acid plant was generating sufficient heat and the acid cooling system was operating the water chillers with no additional electric power required.

An alternate approach (See Section 4.5) to use the refrigeration for maintaining water balance is considered when concentrated acid is available from other adjacent sulfuric acid plants. The available 98 percent acid is simply added to the system to maintain the 93 percent concentration. It should also be noted that in some cases more dilute acid (i.e., 77 percent) may be desired product particularly if it can be used locally such as for leaching purposes. This also would obviate the refrigeration system.

This system uses proven components, design concepts and subsystems but has not been tried even at the pilot plant level. Thus, additional experimental work is required to confirm the concept.

The hot gas heat exchanger design is critical to the operation and could be subject to erosion, tube warpage or oxidation of metal parts. If the design concept is correct, it will not plug.

4.5 ALTERNATE APPROACH TO CONTROL WATER BALANCE

In order to achieve water balance in a sulfuric acid plant, the gas must be substantially cooled to maintain the correct ratio of water vapor volume to SO_2 (SO_3 equivalent) in order to manufacture sulfuric acid. A curve is given on page K-32, Appendix K, which shows the cooling requirements for various gas strengths based on an inlet pressure to the sulfuric acid plant of 600 mm mercury. This is equivalent to approximately 1,500 m (5,000 ft) altitude.

To offset the cost of refrigeration, existing sulfuric acid plants which occasionally use weak SO_2 gases and other plants with an available source of 98 percent or stronger sulfuric acid, can use it as a dehydrating agent. This is accomplished by diluting the 98 percent or stronger acid in the drying tower to make a 93 percent or weaker acid and eliminates the need for refrigeration.

The metallurgical complex located at Torreon, approximately 500 miles north of Mexico, has a total of three sulfuric acid systems. Two plants operate on relatively strong gas and can produce 98 percent sulfuric acid which is normally sent to storage. In 1975, Latisa (a Mexican subsidiary of the Ralph M. Parsons Company) built a sulfuric acid plant for Met-Mex Penolis in Torreon. This sulfuric acid plant has a nominal rated capacity of 500 tons per day of sulfuric acid using lead sintering machine offgas. The sintering machine performance was such that only very weak gases were produced; it did not meet the design levels of 4-1/2 to 6-1/2 percent SO_2 for acid plant feed. There are great extended periods of time in this plant when the gas strength is in the range of 1 to 1-1/2 percent SO_2. During these periods, 98 percent sulfuric acid is pumped from the storage tanks and fed directly into the drying tower pump tank and recirculated over the drying tower. The drying tower acid, after it has been diluted to 93 percent, is then sent to another storage tank which stores the acid.

There have been other cases of using predrying tower acid for achieving water balance in sulfuric acid plants. The Dupont Company in the United States operates a number of ordinance plants and regeneration sulfuric acid plants. These plants decompose acid which is converted into SO_2 and water vapor in the presence of decomposed hydrocarbons. This gas, after being cooled and cleaned, is passed through an electrostatic precipitator and then into a predrying tower. The predrying tower produces a product of 60 Be' (77.67 percent H_2SO_4). If there is a market for this particular grade of acid, then the predrying tower system can be used. Sixty degree Be' acid is one of the old standard product acids which is used in the manufacture of normal superphosphate fertilizer. Additionally, in Europe, Mechim and Lurgi have built sulfuric acid plants with predrying towers which have been used to manufacture weak acid or dirty acids from metallurgical plants. Several of these plants have been built by Mechim for their own use in metallurgical complexes.

One plant which is well known which uses a predrying tower arrangement is in Bor, Yugoslavia. This is about 150 miles southeast of Beograd. In this particular plant, weak SO_2 gas is passed first into a predrying tower and then into a secondary drying tower which operates at the normal 93 to 94 percent acid. The predrying tower produces 60 degree Be' acid (77.67 percent acid). This acid at the Bor complex is used to produce normal superphosphate. Therefore, the technology of using stronger sulfuric acid as a diluting agent to replace refrigeration is known, and there are essentially no difficulties with designing systems to function using this technology.

SECTION 5

FLUE GAS DESULFURIZATION (FGD) SYSTEMS

5.1 GENERAL

Flue gas desulfurization systems may be classified as regenerative and nonregenerative with the former producing SO_2 as a more concentrated gas and the latter generally converting it to a throwaway product. The nonregenerative systems essentially neutralize the SO_2 and place it in a stable form which can then be disposed of without any adverse effects to the environment. Most regenerative systems absorb the SO_2 in a slurry and then regenerate it as a more concentrated stream which can then be used for making either liquid SO_2, sulfuric acid, or sulfur. These products can, in turn, be used to make additional byproducts.

The presently accepted mode of collecting SO_2 in the copper smelting industry is to use a sulfuric acid plant. The gases from fluid-bed roasters and converters are high enough in SO_2 concentration for direct processing in a conventional plant. This is the lowest cost approach to recovering a usable product. However, 0.4 to 1.5 percent SO_2 average concentration in reverberatory furnace offgases is not sufficiently high to directly process in a conventional sulfuric acid plant (refer to Section 4.0). In addition, western copper producers have, from time to time, had difficulties in selling or using internally all of the acid they produce from converters and fluid-bed roasters. In those cases where the sulfuric acid market is such that additional production is not desired, it would seem logical that the nonregenerative systems would be most applicable to controlling SO_2 from the copper smelter reverberatory furnace. In those cases where a usable product is desired, then several possible concentration systems have had sufficient experience at full-scale on reverberatory furnace offgases to be acceptable.

Of the nonregenerative throw-away systems, the one that has received the most use (over 4 years) for collecting SO_2 from copper smelter reverberatory furnace offgases is the lime/limestone gypsum system presently being used on the reverberatory furnaces at the Omahama Smelter in Japan. The gypsum product is sold in Japan. Of all the potential regenerative (concentration) systems that have been considered, the greatest metallurgical gas experience has been with the MgO system used at the Onahama Smelter in Japan and the cold water absorption system at Boliden. The MgO system has been used for over 2 years on their copper reverberatory furnace offgas.

Additional concentration systems that have been operated in metallurgical plants are the citrate and the ammonia systems used to prepare gas for final processing to acid or sulfur. One interesting system that has been used at full-plant scale, but not for metallurgical processing, is the Wellman-Lord sodium double alkali-type system. The double alkali systems may also be potassium or ammonium based and are basically designed to obviate the scaling, plugging, and equipment erosion problems encountered with lime/limestone base scrubbing systems. However, the lime/limestone system experience in Japan on reverberatory furnace offgases and in the U.S. on metallurgical offgases (Duval) would seem to indicate that these latter problems have been solved. However, the double alkali systems retain the capability of regenerating a concentrated stream of SO_2 for production of a usable product.

The product that is the most desirable from a storability and shipping standpoint is sulfur. While there are other successful processes that can produce sulfur from SO_2 containing gas, the only ones that were considered for this study were those using coal as a reductant because of the current and probably future supply problems with gas and oil.

From operating experience with the MgO, and lime/limestone to gypsum, ammonia, and probably the citrate (concentration only) systems on copper smelter reverberatory furnace offgases, it can be said that from a technical standpoint, they are available to control SO_2 emissions. The question that remains, and must be resolved by each individual smelter, is the economic one wherein returns from sales or internal usage of potential products that can result from the system must be compared to costs of disposal as a waste product. This is a very complex decision, as the future acid market, although predicted to increase in the future (see Section 5.11), will also be impacted by fuels desulfurization processes as well as the regenerable flue gas desulfurization systems employed at utility plants.

5.2 LIME/LIMESTONE SO_2 CONTROL SYSTEM FOR REVERBERATORY FURNACE OFFGASES AT THE ONAHAMA COPPER SMELTER

5.2.1 INTRODUCTION

The development of the lime/limestone to gypsum SO_2 control system has been carried out in Japan approximately 20 years at the Hiroshima Technical Institute, one of the three R & D facilities operated by Mitsubishi Metals Company in Japan. During 1968 to 1972, they carried out an extensive program to investigate the scaling problem which was occurring in scrubbers and the mist eliminator of the pilot plant (Figure 5-1).

It was found that preparation and operating conditions of the absorbents were critical to scale formation and required the proper range for pH, temperature, concentration, construction material of the scrubber, L/G, uniformity of the streams, and prevention of carryover mist to the eliminator.

There was some bench scale testing at SO_2 concentrations of 20,000 ppm before the system for the Onahama Smelter reverberatory furnace was constructed. However, no pilot work was done using the higher concentration, and the technology developed for

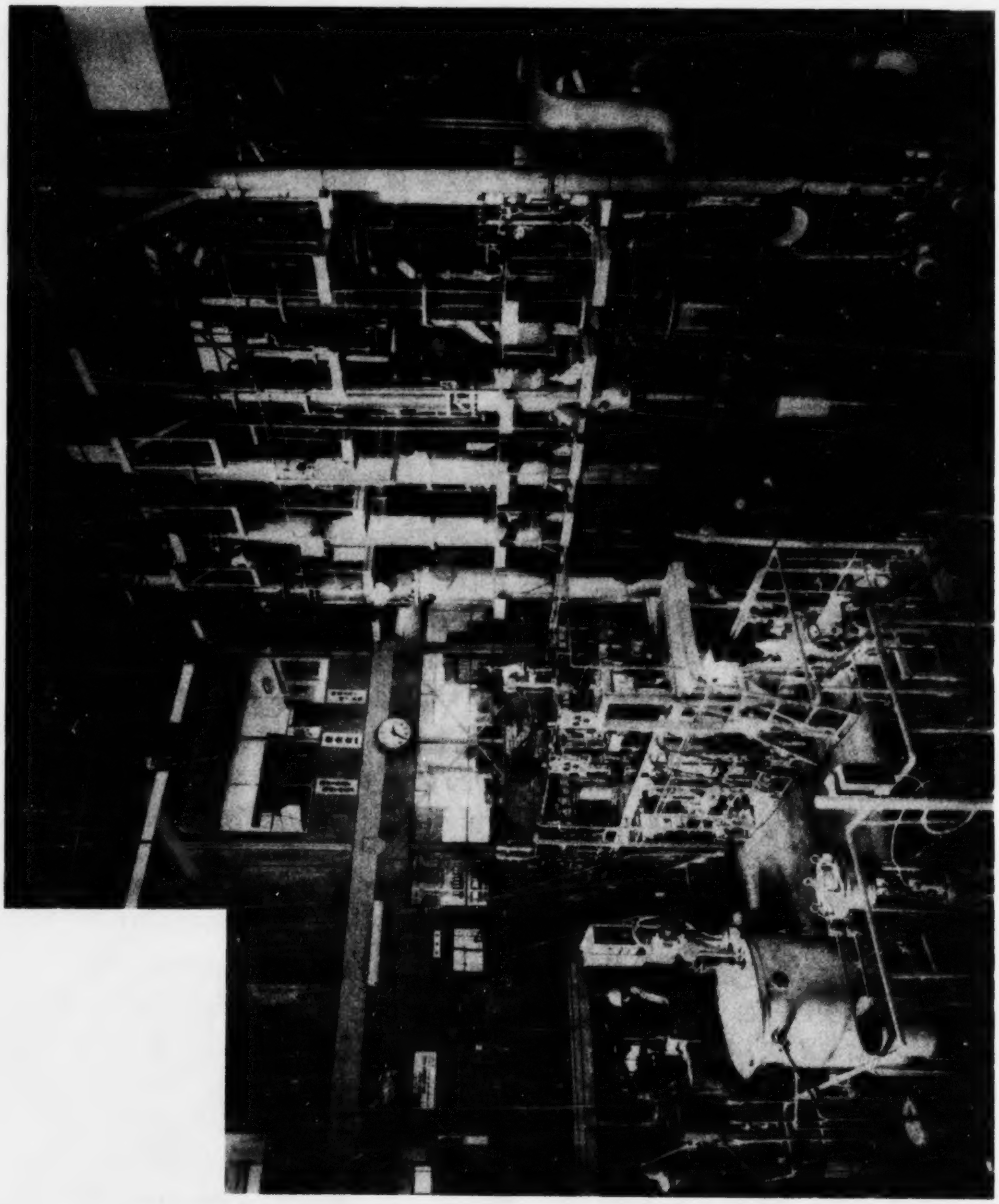


Figure 5-1. Lime/Limestone to Gypsum Pilot Plant

utilities was transferred at that time. Additional discussion of the detailed history of the development of the Japanese lime/limestone system by Mitsubishi is included in Appendix K.

5.2.2 ONAHAMA REVERBERATORY FURNACE FEED

Over 95 percent of the concentrate processed at Onahama is received from abroad. The concentrate is blended in a blending yard or bedding plant and has an average moisture content of 8 percent. When it exceeds 10 percent, the blended mixture is dried in a kiln down to 6 percent. Average concentrate contains 28 percent copper and 28.5 percent sulfur, and matte grade produced is 38 percent.

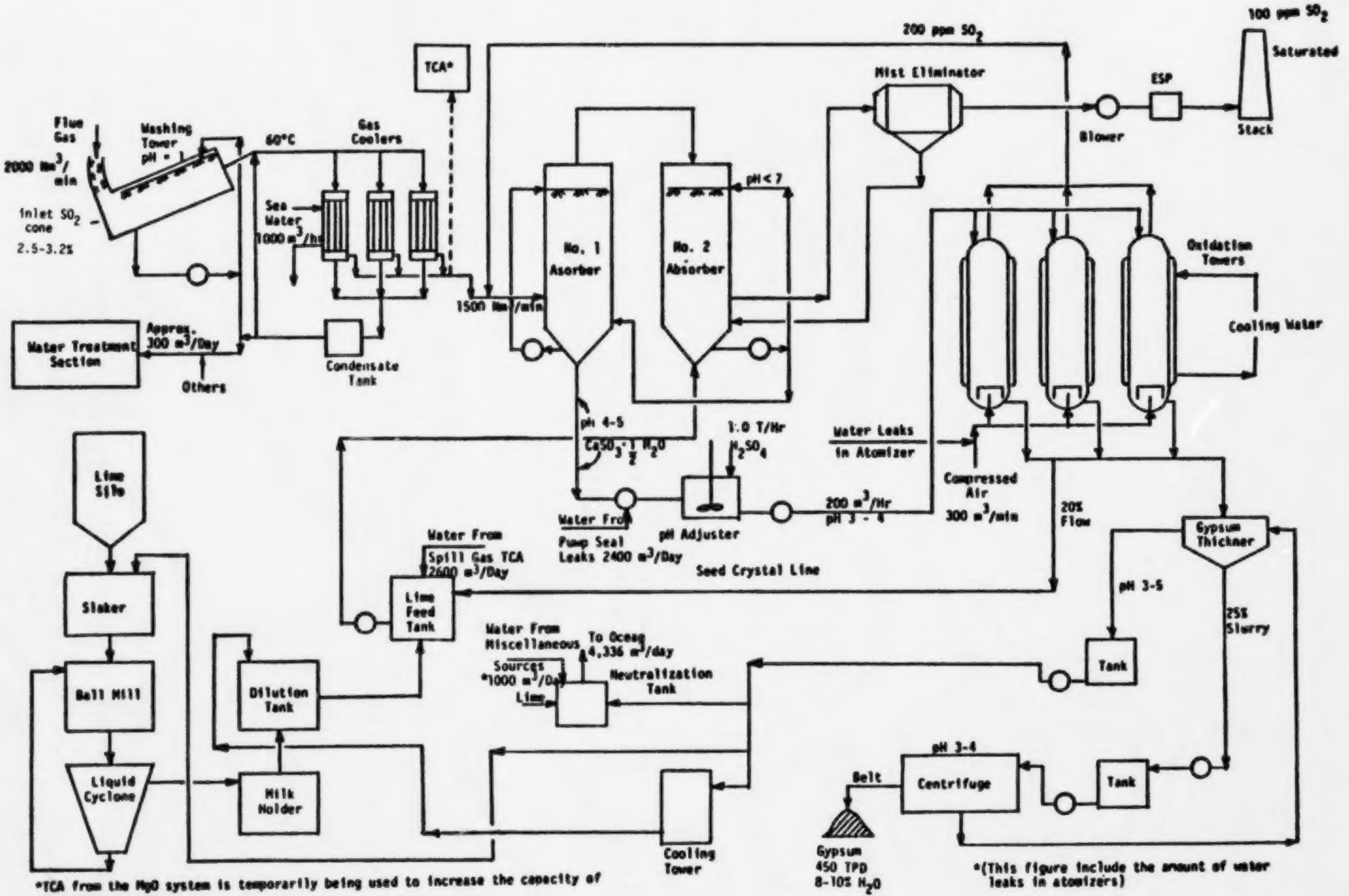
The green charge is transported to the two reverberatory furnaces by the main feed conveyor belt. It is then transferred to furnace distributor belts as needed for furnace charging.

There does not appear to be any effect on SO_2 emissions from the various concentrates processed. They are generally blended into a more or less homogeneous charge mixture.

Description of the reverberatory furnace is included in Section 5. Bed recovery is by bucket loader into bin-type feeders which, in turn, feed the main furnace feed belt. Proportioned fluxes are likewise loaded into other bin-type feeders and added to the main belt at the desired rate. Feed rates are controlled from the main smelter control room.

5.2.3 LIME/LIMESTONE GYPSUM FLOW SYSTEM

Figure 5-2 is a schematic showing the lime/limestone gypsum flowsheet at the Onahama Smelter. The flue gas coming from the reverberatory furnace waste heat boilers and Cottrells enters a wash tower which is a horizontal cylindrical vessel with sprays in both the inlet duct and along the length of the chamber. Simple internal baffles increase the mixing inside the vessel. The flue gas is cooled down to 60°C in the washing tower and then passes to


100 ppm SO_2
Saturated
Stack
ESP
Blower
200 ppm SO_2
Mist Eliminator
TCA*
Flue Gas
2000 Nm^3/min
Washing Tower pH = 1
Inlet SO_2 conc 2.5-3.2%
60°C
Gas Coolers
Sea Water 1000 m^3/hr
Water Treatment Section
Approx. 300 m^3/Day
Others
Condensate Tank
1500 Nm^3/min
No. 1 Asorber
No. 2 Absorber
pH < 7
Oxidation Towers
Cooling Water
pH 4-5
$CaSO_3 \cdot \frac{1}{2} H_2O$
1.0 T/Hr
H_2SO_4
pH Adjuster
Water From Pump Seal Leaks 2400 m^3/Day
Seed Crystal Line
200 m^3/Hr
pH 3 - 4
Water Leaks in Atomizer
Compressed Air 300 m^3/min
20% Flow
Gypsum Thickner
pH 3-5
25% Slurry
Tank
Tank
pH 3-4
Centrifuge
Belt
Gypsum 450 TPD 8-10% H_2O
Lime Silo
Slaker
Ball Mill
Liquid Cyclone
Milk Holder
Dilution Tank
Lime Feed Tank
Water From Spill Gas TCA 2600 m^3/Day
Water From Miscellaneous Sources *1000 m^3/Day
Lime
To Ocean 4,336 m^3/day
Neutralization Tank
Cooling Tower

*TCA from the MgO system is temporarily being used to increase the capacity of the gypsum system

*(This figure include the amount of water leaks in atomizers)

Figure 5-2. Flow Sheet Onahama Lime/Limestone to Gypsum System

5.2.4 DESIGN AND OPERATING CONDITIONS AT THE ONAHAMA SMELTER

5.2.4.1 Input Material and Preparation

The chart in Figure 5-3 shows the SO_2 concentration entering the gypsum plant in the reverberatory furnace offgas. As can be seen, it fluctuates over the period of time shown from a low of 2.1 percent to a high of 2.9 percent. During this operating period, there was no oxygen addition to the reverberatory furnaces. However, both furnaces were operating, and production was nearly 75 percent of normal.

As typical with any reverberatory furnace, the fluctuations result from charging of feed material, slag return and metallurgical reaction. In the first case an excess of SO_2 is generated immediately after charging, and in the second case an opening is presented allowing additional dilution air to enter. As discussed in Section 2.4, this precentage of SO_2 is considerably higher than that reached by U.S. green charge reverberatory furnaces.

Any quick lime (CaO), slaked lime ($Ca[OH]_2$), or limestone ($CaCO_3$) can be used as absorbent. The reaction rate of SO_2 absorption by lime slurry depends on the dissolution rate of the lime. Quick lime will, of course, provide a higher reactivity than slaked lime which in turn provides a higher reactivity than limestone. In the case of limestone it is desirable to crush it into about 300 mesh. Carbide sludge has also been found to be a low cost source of slaked lime and has been used. Quick lime has an effective Ca quantity per ton which is about 1.8 times as large as that of limestone, which of course proportionately minimizes storing and handling requirements.

Absorbent preparation is somewhat different for these systems depending upon whether lime or limestone is used. As noted from the general description of the process by Mitsubishi: "Quick lime is always stored in either large silos or a storage building until ready to be used. It is then transferred to a smaller silo equipped with a gravimetric feed conveyer which meters a fixed amount into

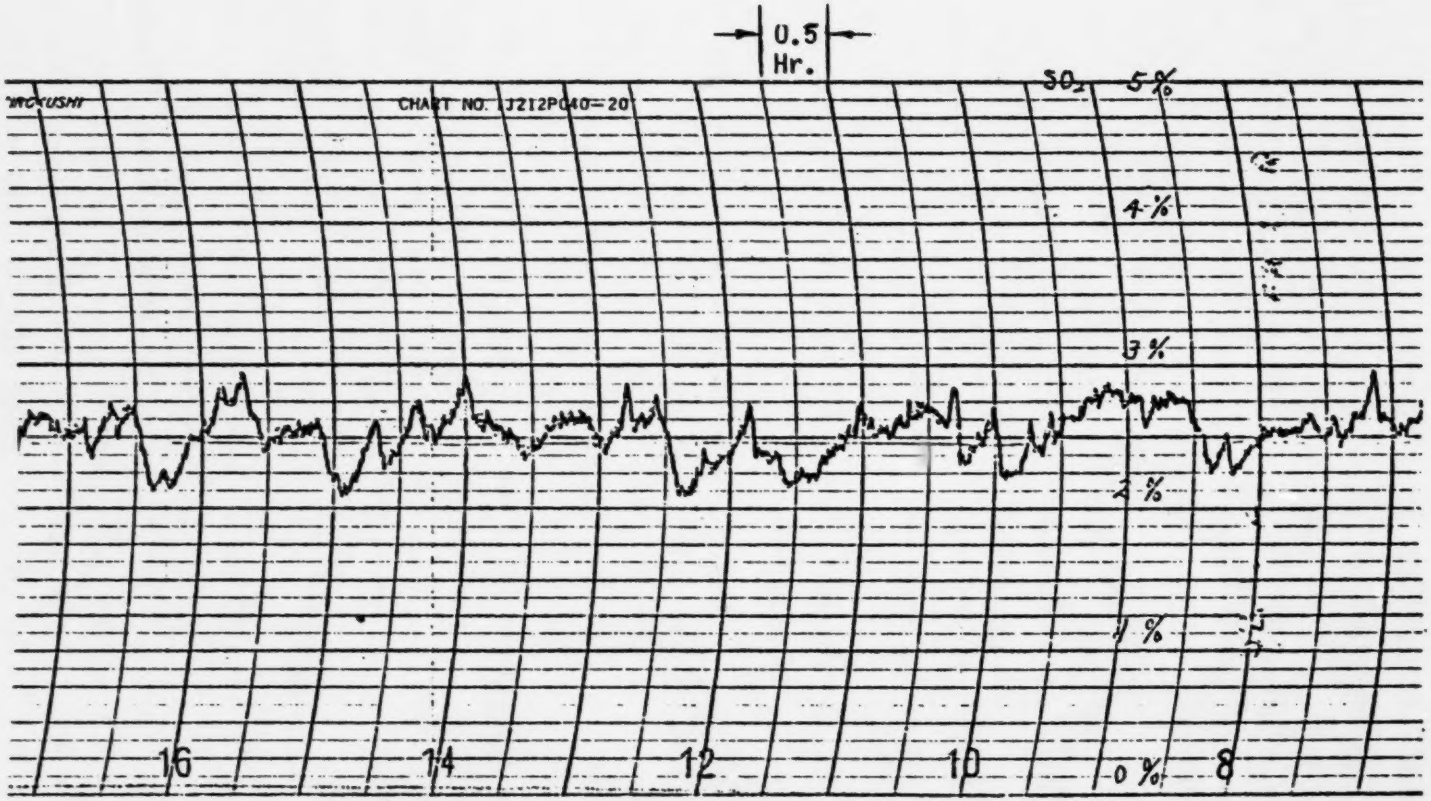


Figure 5-3. ONAHAMA REVERBERATORY FURNACE OFFGAS SO_2 CONCENTRATION VS TIME

five gas coolers. A part of the circulating water is extracted to filter away the collected dust, and the filtrate is returned to the system. The gas coolers are seawater which are indirectly cooled heat exchangers that further cool the gas. The seawater is returned to the ocean.

The gas at this point may be separated, and part goes to the MgO system and part goes to the following gypsum system. At the present time, the MgO system is not being used, but the TCA scrubber in the MgO system has been connected as an additional absorber to allow processing of a larger quantity of gas. The two systems were originally designed to handle the total offgas from the two reverberatory furnaces. These furnaces are presently operating at reduced capacity, and the lack of demand for acid has eliminated the need for the MgO system.

Following the main cleaning system, the gas goes to the No. 1 absorber and then to the No. 2 absorber, each absorbing approximately half of the SO_2 entering the system. It then goes to the mist eliminator, the blower, a precipitator, and finally the stack. There is no exhaust gas reheat. The blower is the main reverberatory furnace blower and provides suction for the entire system which therefore operates at negative pressure to this point.

The absorbent flow rate through the No. 1 absorber is approximately half of the absorbent flow rate of the No. 2 absorber. A series of six centrifugal pumps are used to pump the 10 percent slurry absorbent in the No. 2 absorber circuit and a series of three pumps in the No. 1 absorber-absorbent circuit. The large number of pumps is used because of an installation space problem.

The calcium sulfite slurry is taken from the No. 1 absorber at pH 4-5 and pumped into a pH adjuster where acid is used to adjust the pH to 3-4. Approximately 200 m^3 per hour flows to the three oxidation towers. A special rotary atomizer is used to mix the compressed air entering the oxidation towers with the slurry. The oxidizing towers are indirectly cooled as required.

From the oxidizing towers, the gypsum slurry flows to the thickener and approximately 20 percent of the flow goes to the lime tank to supply seed crystals. The seed crystals enter the absorption system in the No. 2 absorber. The addition of seed crystal gypsum provides a sacrificial surface for crystal precipitation greatly reducing and controlling deposition on absorber surfaces.

The underflow from the gypsum thickener flows as a 25 percent slurry to a tank through the pumps and then into a bank of 14 centrifuges at a pH of 3-4. From the centrifuges, the gypsum passes through a belt to storage for shipment. The liquid from the centrifuges passes back to the gypsum thickener.

The overflow from the gypsum thickener passes to a tank and pump and then to either a cooling tower and the slaking system or directly into the slaking system. The thickener overflow is used for slaking of the lime in the slaker. The slaked material then flows to a ball mill and a liquid cyclone. The heavy material from the liquid cyclone is passed back to the ball mill. Then, the light material, which is lime milk, is then passed to the milk holder and into the dilution tank. From the dilution tank, the material goes to the lime seed tank and back into the No. 2 absorber.

Excess water from the thickener overflow goes to the neutralization plant where lime is added to obtain a pH of 7 and then to the ocean. Water enters the system from pump seals, the spill gas TCA from the smelter, collection systems, the oxidizing tower atomizers, and the gas from the reverberatory furnace. Condensate from the gas coolers is sent to the water treatment section or it may be used in the system if required. A more detailed description of individual components is included in Appendix M.

the lime slurry tank. Recycled water from the gypsum recovery section is mixed with the lime to prepare a constant weight percent slurry to be used as absorbent makeup." Sizing of the lime particles by grinding (ball mill in slaking section) is necessary to produce the proper pH because of the reactivity of the material.

The limestone equipment required depends on the size of the limestone commercially available to the scrubbing plant and the physical distance between the limestone storage area and the absorbers. Since a 325 mesh limestone powder is desired for the gypsum production case,a ball mill grinding operation is necessary.

Generally, the limestone is ordered based on what is available from the vendor. They maintain fairly tight specifications on the particle size. The limestone is ordered to have the finest particle size available without specifying the exact number. If this number were specified with a stricter requirement, it would probably double the cost. Presently, the limestone received as a slurry by Onahama is in the range of 200 to 500 mesh.

The lime or limestone composition or the ratio of calcium oxide to calcium carbonate will affect cost. The limestone obtained in Japan is approximately 57 percent CaO indicating a very pure material. As impurities increase, generally the cost of the limestone decreases.

For a new application to a smelter it would probably be advisable to begin with the maximum amount of CaO and to decrease gradually to determine the final workable ratio under the specific conditions. Presently, the mole ratio of CaO to $CaCO_3$ is approximately 50 percent.

Corrosion tends to occur when chlorine or chlorides enter the system. The initial cooler, which is a spray chamber, tends to wash out these materials. Chlorine, up to a maximum of 1,000 ppm in the liquid phase from the cooler, will not cause corrosion.

Trace metals may be contained in the flue gas entering the system and may include copper, cadmium, lead, chromium and arsenic. Also, zinc, magnesium and sodium may be present.

The following materials are used at Onahama at the rate specified:

- CaO is 7.3 tons per hour as calcium hydroxide
- H_2SO_4 is 0.1 tons per hour
- Electric power required is 230 kWh per ton of product which includes blowers, pumps, and associated equipment - this averages 4,000 to 5,000 kWh
- Compressed air is 300 standard cubic meters per minute
- Cooling, pump seal, and miscellaneous water (sea and fresh) is 6,000 to 8,000 m^3 per day.

5.2.4.2 Internal Operating Conditions

The flue gases are prequenched in the flue gas cooler to approximately the adiabatic saturation temperature by evaporation of water sprayed into the system. The gases are cooled to approximately 60°C and then sent to gas coolers for further cooling. This additional cooling is required to maintain absorption efficiency. The temperature of the gas remains essentially constant until it reaches the stack. No stack reheat is done at the Onahama Smelter because apparently the visible water vapor from the stack is not objectionable to the local residents.

After the flue gas has been prequenched, it enters the first absorber where lime and limestone slurry is sprayed through spray nozzles located at the top of the absorber. The pH of the slurry at the circulation pump discharge is controlled by adding makeup lime/limestone slurry to the circulation tank.

As the flue gas passes through the absorber, some droplets of slurry are entrained. These drops are removed by using a chevron plate-type mist eliminator. Recycled water from the neutralization plant is used for continuous washing of its surfaces.

The relative SO_2 absorption between Nos. 1 and 2 absorbers has changed as experience has developed. Presently, it is closer to a 50 to 50 percent relationship. The pH of the absorbent is generally less than seven in both absorbers.

It has been found that scaling or crystalization of the calcium sulfite occurs as either many small crystals, as a layer on the surface of equipment, or as layers built on seed crystals. If the formation of the calcium sulfite can be controlled to a rate below the rate of crystal growth on the seed crystals, then the crystal nucleation will preferentially go to these seed crystals. However, if the calcium sulfite rate of formation exceeds the rate of crystalization on the seed crystals, or if there are not sufficient seed crystals present, then crystalization will occur either as scaling on the surface of the equipment or as formation of small new freestanding crystals. Thus, for a given solubility of calcium sulfite, the concentration of calcium sulfite in the liquid phase must be controlled. This can be done by controlling either the L/G in the absorber or the flow rate of the seed crystals to the absorption circuit. According to the above theory, the lower the SO_2 concentration, the less scaling will occur.

Because of the scaling problem and also because of the fluctuation of the SO_2 concentration, design of the internal conditions of the system is critical (see Figure 5-3). There has not been any serious problems with operation of the gypsum system within the range of fluctuations occurring at the Onahama Smelter. However, the following design considerations (Mitsubishi considers the details of some of the following to be proprietary) must be optimum to provide a flexible system:

1. Selection of the optimum slurry velocities in the piping
2. Proper application of instrumentation
3. Optimum equipment selection and application
4. Special piping features in the problem areas

During operation, the size of gypsum crystals, and scaling are controlled by the following:

- The pH of the slurry
- The temperature of the slurry
- The speed of oxidation (air pressure)

Size of the crystal does not affect plugging or scaling. The gypsum board manufacturers require large crystals. Large crystals are easily centrifuged, but the smaller size is more difficult to separate in the centrifuge causing a higher water content in the gypsum. Also, small size tends to produce vibration.

The pH of the slurry is controlled very closely as it leaves the absorption system and enters the oxidation towers at 3 to 4. The percent SO_2 leaving the oxidizer is less than 200 ppm. When sulfuric acid is used to control pH, there will be an increase in SO_2 at this point which can be variable. Speed of oxidation is controlled by the pressure of the oxidizer, nominally 43 psi (3 kg/cm^2 gauge).

The lowest pH occurs at the oxidizer tower, and the first gas cooler. The gas cooler pH is less than one. The slurry leaves the thickener at approximately 3 to 5 and enters either the slaking system or goes out to the neutralization tank where it is modified to a pH of 7 before leaving for the ocean. The fluid leaving the gypsum centrifuge has a pH of approximately 3 to 4.

5.2.4.3 Output Conditions and Materials

- Output SO_2

The chart in Figure 5-4 shows a trace of output SO_2 versus time for the gypsum system. Output varies from 0 to a maximum peak of 133 ppm with the average approximately 40 to 60 ppm.

- Gypsum

The gypsum crystals are controlled to meet the requirements of the wall board manufacturers. Generally, a crystal shape which is bulky is desired to minimize adhered water (see Figure 5-5).

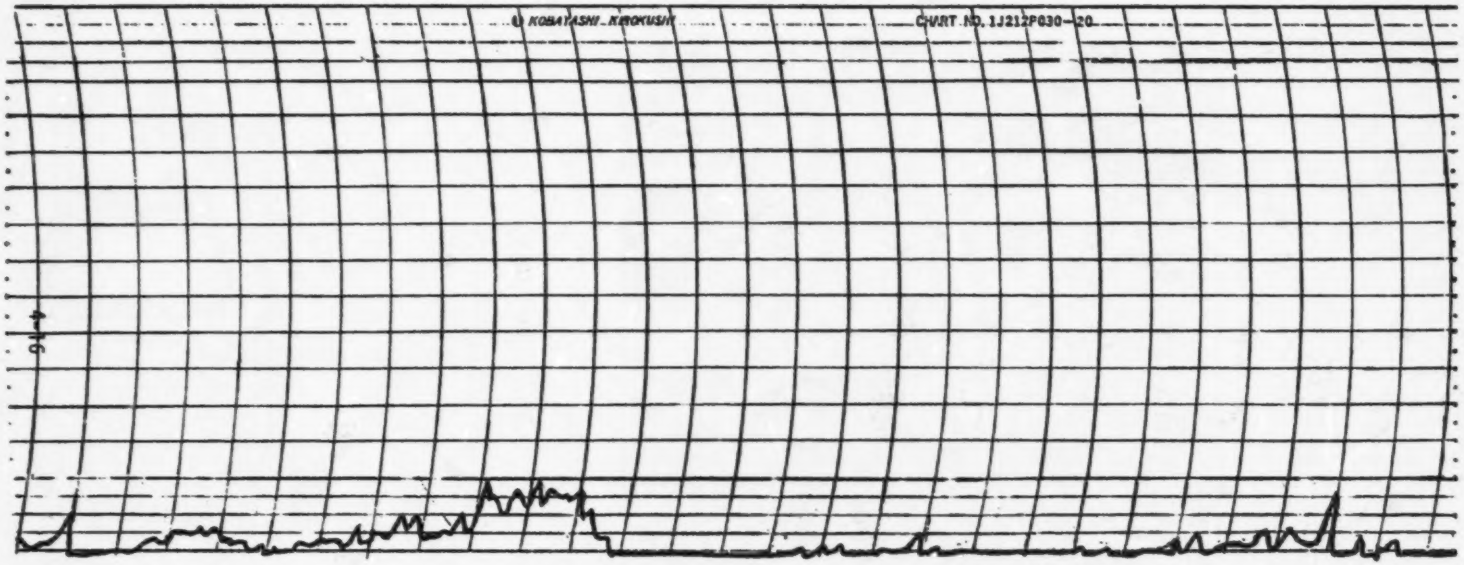
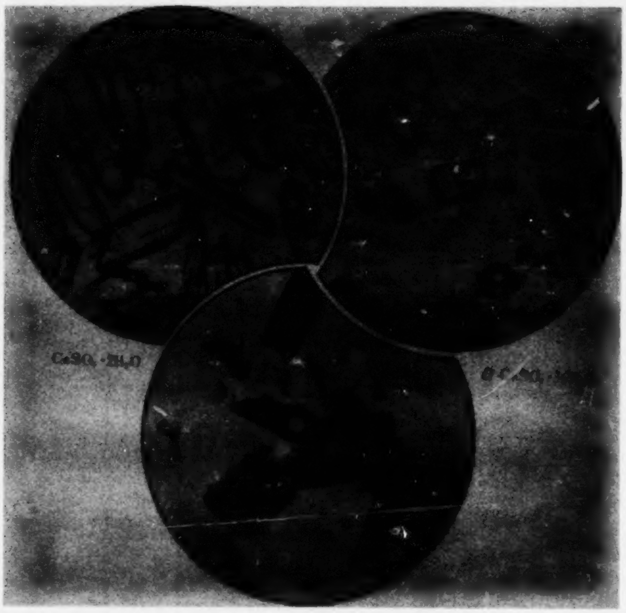


Figure 5-4. ONAHAMA LIME/LIMESTONE GYPSUM SYSTEM OFFGAS SO_2 CONCENTRATION (FULL RANGE 1000 PPM)


$CaSO_4 \cdot 2H_2O$

Note: (200x) $CaSO_4.2\ H_2O$ (left), $CaSO_4.1/2\ H_2O$ (right), $CaSO_3.1/2\ H_2O$ (bottom)

Figure 5-5. Crystal Comparison

If the crystals are large and bulky they have a low surface-to-volume ratio which minimizes external water content. The long crystals are desirable from a strength standpoint but do tend to have an excess in associated water. The production at Onahama varies from 5 to 10 percent adhered water and is approximately 98 percent pure gypsum. For the cement industry, color or impurities are important factors. If the crystals are very slightly yellow, this tends to relate to larger size crystals. If the crystals are all white, they tend to be smaller in size. Figure 5-5 shows photographs of $CaSO_4 \bullet 2H_2O$, $CaSO_4 \bullet 1/2H_2O$, and $CaSO_3 \bullet 1/2\ H_2O$ crystals at 200 to 300 times magnification. The calcium sulfate crystals with one-half molecule of water are considerably smaller than those with the two water molecules. The bulk $CaSO_2 \bullet 2H_2O$ are the desired configuration.

The chemical requirements for the gypsum are as follows:

- CaO - 32.5 percent b.w.
- SO_3 - 45.8 percent b.w.
- Residual CaO less than 0.1 percent.

Almost continuous inspection of the gypsum crystals produced by the gypsum system is maintained. A microscope of 200 to 300 magnification is located in the gypsum system control room, and slides of the product are made and viewed at this point. The microscope used is a standard metallurgical microscope and has a polaroid camera attachment for taking instant development pictures which are taken once or twice each shift. When the crystals do not appear to be the proper shape the system is adjusted, but there is a considerable lag time between the adjustment and the change in the product. Material unsuitable for wallboard is most likely sold to cement manufacturers.

Magnesium of 1 percent (usually 0.2 percent as magnesium oxide) is the maximum allowable in the wall board gypsum. The silicon dioxide is usually less than 1 percent, but it is not too critical.

- Water

A schematic of the wastewater treatment plant at the Onahama Smelter is shown in Figure 5-6. This system receives waste from the acid, the gypsum, and the magnesium oxide plants as well as the general wastewater plant.

From the receiver tank, the effluent goes to a mixing tank where milk of lime is added. This is followed by three neutralizing tanks allowing the material to reach a pH of approximately 7. From the neutralizing tanks, the fluid goes to a tank where coagulant is added and is then passed to a thickener.

The underflow from the thickener goes to a centrifuge and this solid material is then taken to the reverberatory furnace. The overflow from the thickener goes to a tank where milk of lime is added, and further neutralization occurs with sodium hydroxide in the two following tanks to reach a pH of between 11 and 12. In the following tank, organic coagulant is added and this is then passed to another thickener.

The underflow from the second thickener goes to filter presses, and the solids are then taken to the reverberatory furnace. The overflow from the thickener passes to two settling pits and eventually on to the ocean.

- Trace Metals

Trace metals are handled so as to cause them to go out in the reverberatory furnace slag. The dust from the reverberatory furnace Cottrells goes to the local zinc plant where the trace metals are removed. Lime is added to the water treatment plant to control pH, COD, total suspended solids and trace metals. In addition, the following materials are checked to determine if they are present: zinc, copper, manganese, fluorine, total chromium, lead, arsenic cyanide, phosphorus, nickel, soluble iron, cadmium, hexavalent chromium. Arsenic may be as high as 50 ppm in the concentrate, however, it generally averages only 3 ppm.

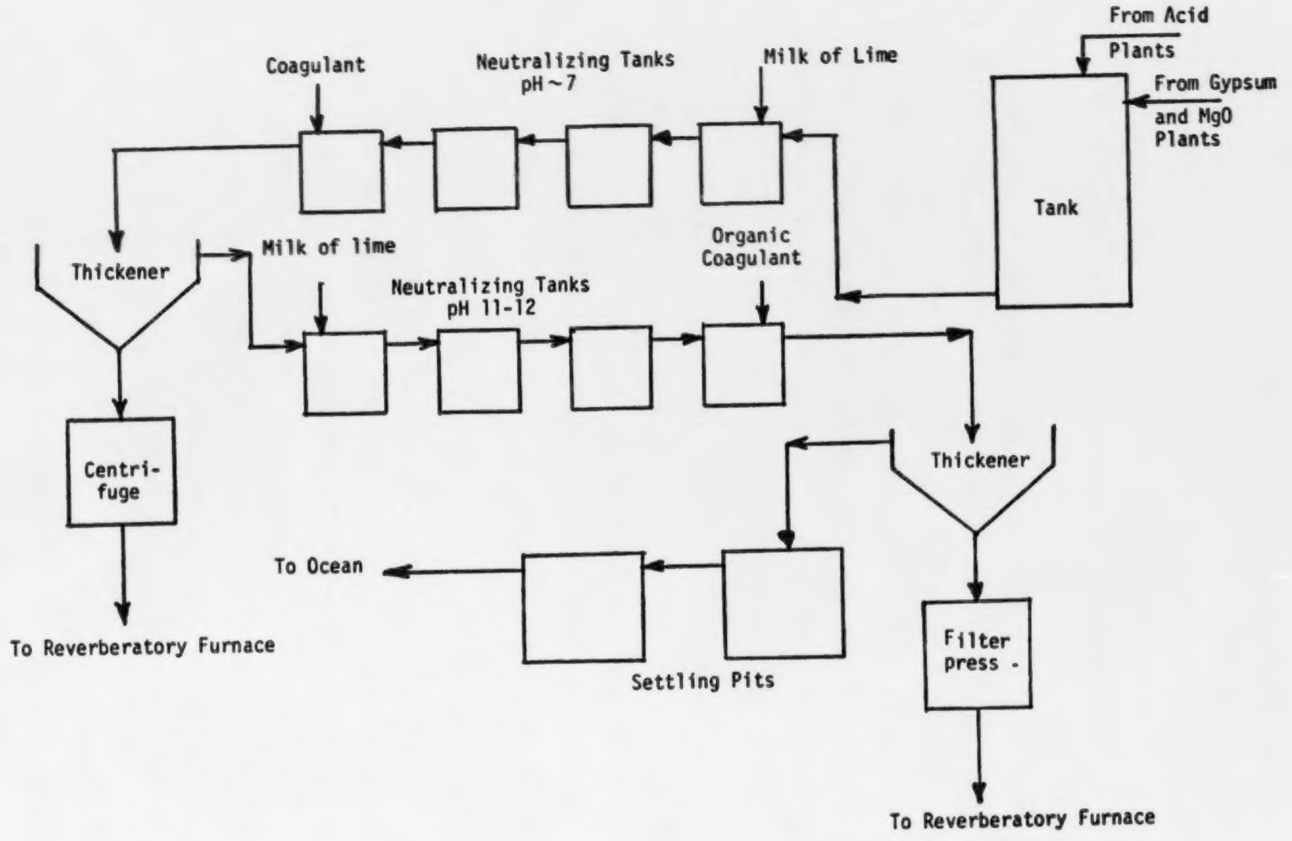

From Acid
Plants
From Gypsum
and MgO
Plants
Tank
Milk of Lime
Neutralizing Tanks
pH ~ 7
Coagulant
Thickener
Centri-
fuge
To Reverberatory Furnace
Milk of lime
Neutralizing Tanks
pH 11-12
Organic
Coagulant
Thickener
Filter
press -
To Reverberatory Furnace
Settling Pits
To Ocean

Figure 5-6. Schematic of Onahama Wastewater Treatment Plant

The first stage in the water treatment plant (where pH of 7 is controlled) in effect reduces the $Ca(CO_3)$ to calcium sulfate, water and carbon dioxide. The second stage (where pH of 11 is obtained with sodium hydroxide and impurities such as cadmium, arsenic and copper are precipiated out) is very near the optimum range from this precipitation. Professor Tozawa of Tohoku University presented a paper at a symposium on water treatment in Sendai, Japan, on January 20, 1977. This data is shown in Figure 5-7. This indicates that the best pH for precipitating arsenic as $Ca_3(AsO_4)_2$ is from 11.7 to 13.0 under the conditions where Ca·As(V) molal ratio is 3 to 1 or higher. The higher molal ratio is preferred to reduce the Ca(V) concentration in the solution. This statement agreed well with the operational conditions of the Onahama water treatment plant where the end of the second series of neutralization (alkalization) is maintained at the pH close to 12.

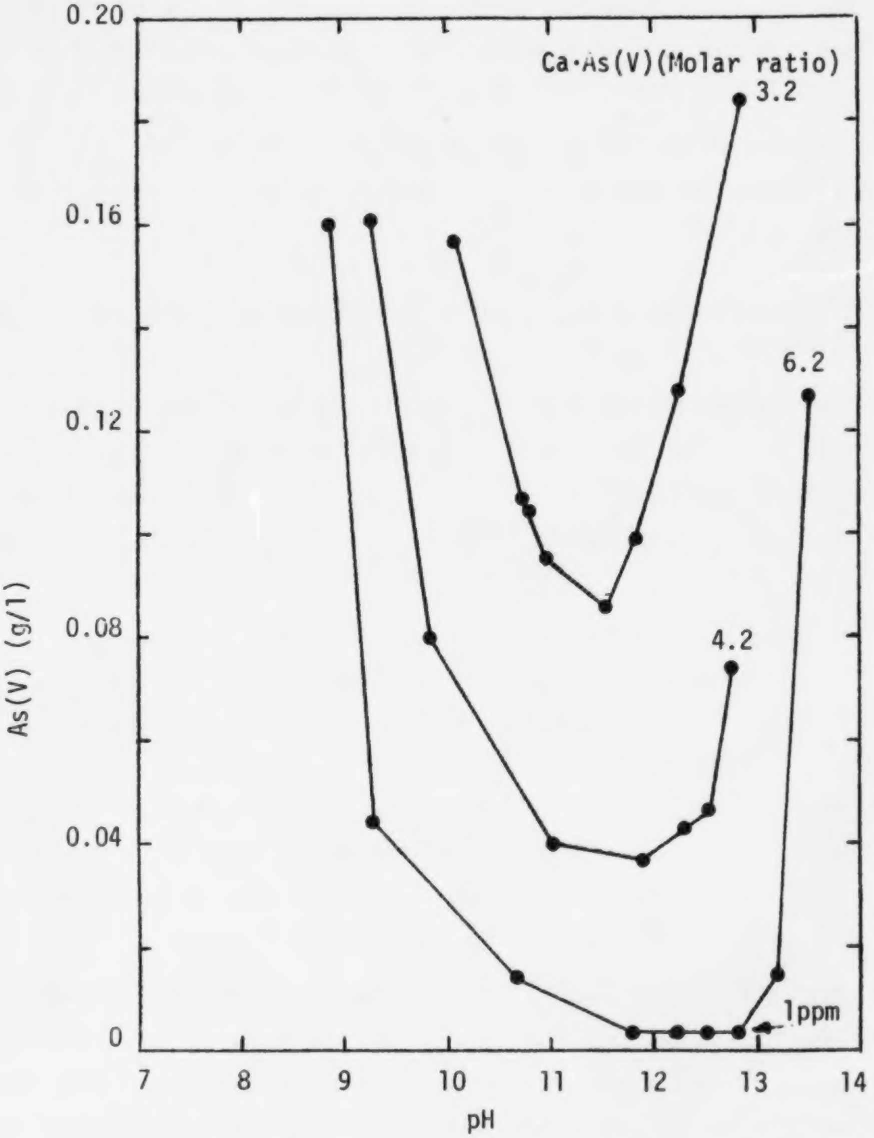
It is also of interest to note that heating $Ca_3(AsO_4)_2$ to 600°C or higher in air makes this compound more stable so that it will not leach out even in media having pH 7-14. This technique is practiced at the Hibi Smelter of Mitsui Metals and Mining Company in Japan, but has not been attempted at Onahama.

5.2.4.4 System Cleaning

The absorption towers are cleaned of scale once every 6 months. These are washed down with water for approximately 10 hours. The plastic grid packings are removed and physically scrubbed. The scale generally is relatively soft and comes off easily. Likewise, the mist catcher is cleaned two times a year at the same time as cleaning of the absorption towers. This device is cleaned by high pressure water sprays as required.

5.2.4.5 Plant Area

The area required for the Onahama gypsum system is approximately 65 by 40 m or 2,600 m^2. This is exclusive of the compressor house, the gypsum storage house, and the slaking section which could add another 2,000 m^2.



Initial As(V) = 1.0 g/1. at room temperature 1 hour

Figure 5-7. ARSENIC PRECIPITATION CONDITIONS

5.2.4.6 Operating Personnel

The gypsum system, the MgO plant, the water treatment plant, and the spill gas handling system are operated by a crew of five men and one foreman for each shift. In addition, a maintenance crew of three people is used. This would then require 27 people.*

The entire pollution control effort at the smelter uses a total crew of approximately 40. This compares to 200 for the smelting operation.

5.2.5 APPLICATION OF THE ONAHAMA LIME/LIMESTONE SCRUBBING SYSTEM TO U.S. SMELTERS

The gypsum system used at Onahama was one of the early ones designed so it included pumps with water seals which require a relatively large amount of water. Approximately 2,400 m^3/day is required for pump seal water. Present designs do not use this type of pump seal.

Washing tower water of approximately 300 m^3 per day goes to the water treatment section. The oxidizer towers use approximately 300 m^3/day for atomizer seals and this also goes into the system. Compressor cooling, blower cooling, and miscellaneous water usage such as cleaning shoes and so forth uses an additional 1,000 m^3/day. The gas coolers use 1,000 m^3/hr maximum and of course this cooling water could be recycled. A total of 6,000 m^3/day of water goes to the ocean after treatment in the neutralization tank.

The actual water lost, if the system were designed to reduce or minimize this factor, is that going out the stack at saturated condition and that in the gypsum. This is approximately 48 m^3/day for the Onahama Smelter. Miscellaneous water would be an addition to this. Input water that could be available is that entering the system in the flue gas. Appendix M presents calculations for the water balance at the Onahama Smelter under the present operating conditions of 2,000 Nm^3/min (70,600 scfm) showing sources and emissions of water which can be summarized as:

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*(5+1) x 4+3 = 27

Water in flue gas	593 lb/min
Water in gas at outlet of washing tower	785 lb/min
Water in gas at outlet of gas coolers	333 lb/min
Water removed from flue gas	453 lb/min
Water entering washing tower	192 lb/min
Water entering system from pump seals	3,673 lb/min
Water entering system from atomizer seals	459 lb/min
Water entering system from spill gas TCA	1,613 lb/min
Water entering system from miscellaneous sources	1,071 lb/min
Total water entering system 333 + 3,673 + 459 + 1,613 + 1,071 =	7,149 lb/min
Water leaving neutralization tank	6,636 lb/min
Water leaving cooling section	333 lb/min
Water leaving with gypsum	180 lb/min
Total water leaving system = 9,186 + 198 + 459 (Exclusive of evaporation and purge losses)	7,149 lb/min

With a system designed for minimum water use, at least the following must be accomplished:

1. Selection of equipment such as pumps and rotary atomizers to use water as little as possible (minimize seal requirements).
2. Minimizing the amount of water to be treated at the water treatment plant by reducing the dust load in the gas at the inlet of such plants.
3. Separation of gypsum saturated water and non-gypsum containing water.
4. Multi-utilization of water by recycling from the water treatment plant.

The following projected water balance is estimated, assuming the above factors are implemented:

Water in flue gas entering gas conditioning system	593 lb/min
Water in flue gas leaving gas conditioning system, W_{gc}	269 lb/min
Water loss in washing tower and gas cooler section, W_e (assume 10 percent purge and 20 percent evaporation)	81 lb/min
Water leaving in gypsum, W_g	198 lb/min
Water lost by evaporation, W_s	735 lb/min
Total water out of the gypsum system W_{et}	
$W_e + W_g + W_s = 81 + 198 + 735 =$	1,014 lb/min
Total water required (not including miscellaneous)	
$W_{et} - W_{gc} = 1,014 - 269 =$	745 lb/min (90gpm)

The limestone in Japan is a very pure material with practically 100 percent $CaCO_3$. It assays at approximately 57 percent CaO which could indicate that even some of the carbonate has weathered away. In the U.S., limestone is never pure calcium carbonate, but always contains variable percentages of foreign matter usually magnesium carbonate, clay, silica, compounds of iron and aluminum, and frequently fossil remains. Limestone is mined in all but three or four of the states with Ohio, Illinois, Pennsylvania, New York, and Michigan in the order named leading in production of broken stone for all technical purposes. More than half is used in the construction of roads and in making concrete. Large amounts are utilized as a flux in separating metals from their ores and in powdered form for neutralizing the acid present in certain soils. It is the source of all commercial lime and in addition has numerous minor uses. In large quarried rocks, it is our principal building stone.

Large quantities of limestone are located in Arizona. Analysis of this limestone varies, but typically contains 50 to 52 percent

CaO approximately comparable to that used at Onahama at 57 percent. Magnesium content may vary from that of dolomite to essentially none. Other constituents such as silica can vary significantly from deposit to deposit.

The Gypsum Association of Los Angeles was contacted to determine the market for gypsum in the Western United States (west of the Mississippi). They stated that gypsum is mined in California, Nevada, Utah, Iowa, southern Oklahoma, Texas, Arizona, and New Mexico. There is substantial quantities of gypsum produced as a byproduct from the chemical industry and power plants, and the market for gypsum at the present time is not very encouraging. Gypsum is open pit-mined in Arizona near Hayden so it would seem that if it were produced as a product from pollution control facilities, it would have to be sold at a price that would at the very least, compete with existing mines.

Considerable effort has been expended to reduce the infiltration air into the furnaces by leakage point elimination (refer to Section 3.0). The SO_2 concentration from these furnaces is considerably higher than that reported by U.S. smelters. The lower concentration would actually be beneficial to the operation of a lime/limestone gypsum system although it would, of course, result in higher volume flows since it is caused by infiltration air and furnace operations.

Considerable improvement in system design and development of operational know-how has occurred at the Onahama Smelter during the startup and subsequent operation of the gypsum system. It is this detailed experience that the Mitsubishi Metals Corporation personnel feel is absolutely essential to operate the gypsum plant without plugging and other troubles.

There has been no experience with the gypsum system treating coal-fired reverberatory furnace offgases. As the amount of carbon dioxide in the gas may increase, the $CaCO_3$ scale phenomena in the $Ca(OH)_2$ milk absorbing system could change.

It is believed that there would be no major problems when applying the gypsum system to calcine charge reverberatory furnace offgases. On the contrary, it would present a favorable condition to the design and operation of the plant because of the reduced concentration of SO_2.

5.3 DUVAL SIERRITA LIME SCRUBBER SO_2 CONTROL SYSTEM

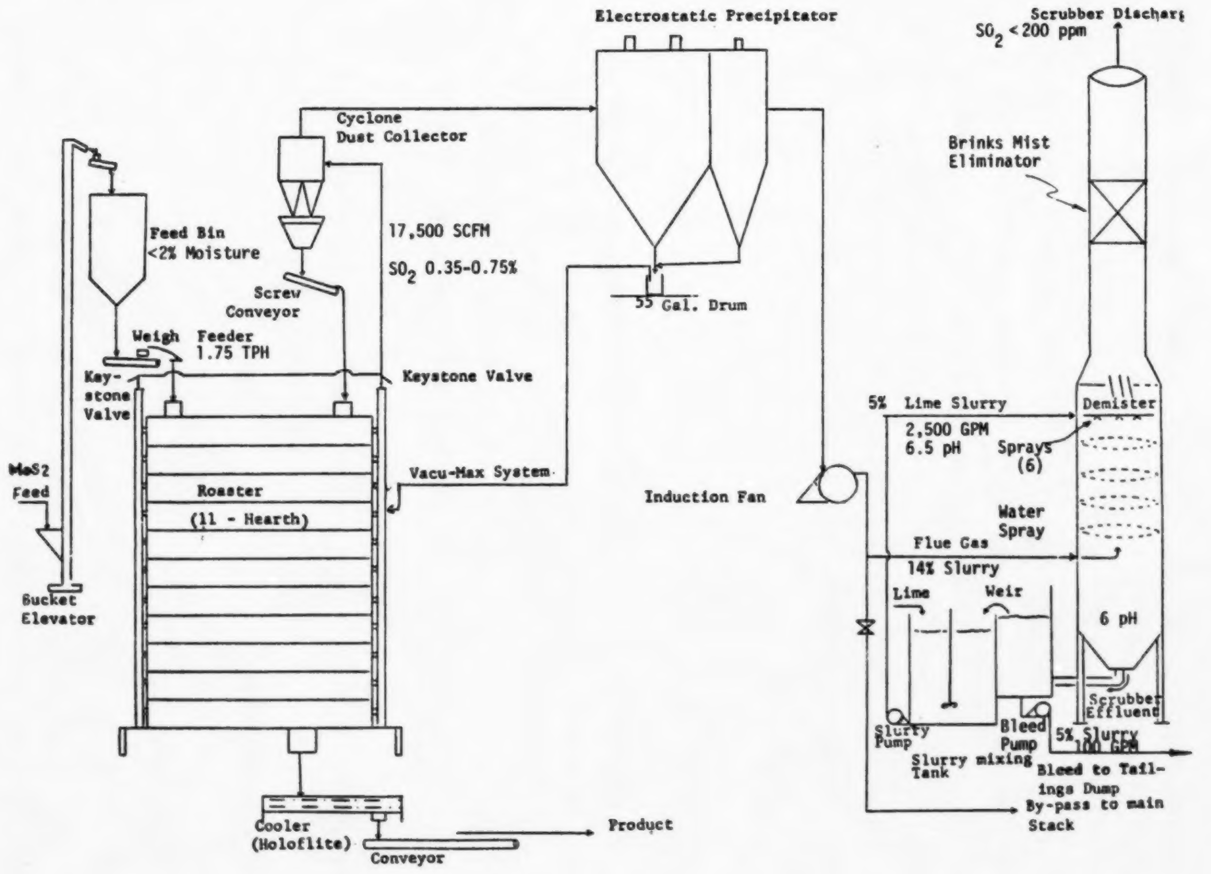
5.3.1 INTRODUCTION

A lime slurry sulfur dioxide scrubbing system is currently being operated to control offgases from two multihearth roasters processing molybdenum copper ores at the Duval Sierrita Company processing plant near Tucson, Arizona. The scrubbing system receives gases containing 0.35 to 0.75 percent SO_2 concentration and treats them to emit gases to the atmosphere at less than 200 ppm.

This SO_2 control system has been under development since 1968. At that time, the company made an extensive survey to select an SO_2 control system to treat the offgases from the roasters. The system was designed and implemented in late 1970 and had continuing difficulties until approximately 1973. The development effort resulted in an improvement from 65 percent availability to the present 95 percent availability. Sulfur dioxide removal efficiency is in the range of 92 to 96 percent.

5.3.2 SYSTEM DESCRIPTION

Figure 5-8 is a schematic showing the roaster and scrubbing system flowsheet. Each roaster has an identical parallel system. The roaster offgases are first passed through a series of four cyclone dust collectors. After passing through the system to the precipitator inlet, the temperature is reduced. The electrostatic precipitator is at least 99.5 percent efficient and cleans the gases of the remaining particulate. The gases are then passed directly into a TCA type scrubber. The temperature is reduced by spraying in water to ensure di-


Electrostatic Precipitator
Scrubber Dischar
SO_2 < 200 ppm
Cyclone
Dust Collector
Brinks Mist
Eliminator
Feed Bin
<2% Moisture
17,500 SCFM
SO_2 0.35-0.75%
Screw
Conveyor
55 Gal. Drum
Weigh Feeder
1.75 TPH
Key-
stone
Valve
Keystone Valve
5% Lime Slurry
2,500 GPM
6.5 pH
Demister
Sprays
(6)
MoS2
Feed
Vacu-Max System
Roaster
(11 - Hearth)
Induction Fan
Water
Spray
Flue Gas
14% Slurry
Lime
Weir
6 pH
Bucket
Elevator
Scrubber
Effluent
Slurry
Pump
Bleed
Pump
5% Slurry
100 GPM
Slurry mixing
Tank
Bleed to Tail-
ings Dump
By-pass to main
Stack
Cooler
(Holoflite)
Conveyor
Product

5.8 DUVAL SIERRITA ROASTING-SCRUBBING FLOWSHEET (One Side of Duplicate System) mensional stability of the 7 gram polypropylene balls used as the mixing medium in the scrubber.

The gases pass through three stages of balls presently at a 6-in stagnant thickness for each layer. The lime slurry is sprayed downward countercurrently to the gas flow through six spray nozzles. After passing through the three ball stages, the gases then go through a vane type demister before leaving the scrubber. A Brinks mist eliminator follows the scrubber and was included in the system to improve the removal of the acid mist. A fan is located downstream of this mist eliminator at the base of the stack. The exit temperature out the stack is approximately 114°F, and the exit gas varies from 100 to 200 ppm of SO_2.

5.3.3 INPUT CONDITIONS

The mined ore contains both copper sulfide and molybdenum disulfide. These two materials are separated by flotation. The copper sulfide is sent to an outside smelter for further processing. The molybdenum sulfide is processed in the roaster. The feed to the roaster contains approximately 50 percent molybdenum and 35 percent sulfur.

Approximately 10 to 15 percent of the total molybdenum disulfide is sold directly as a product. The remainder is processed in the roaster to form molybdenum trioxide.

5.3.4 INTERNAL PROCESSING

There are 11 hearths in the roaster with the upper two hearths fired by gas burners to supply ignition heat. Once the molybdenum disulfide reaches ignition temperature, it burns by itself to oxidize most of the sulfur. The lower four hearths also have burners which are used to drive off the last 1 percent of the sulfur. Excess air is injected into the multihearth roaster which operates at an average feed rate of 1.7 ton/hr.

The gases from the roaster entering the scrubber contain the following:

O_2 - 19%
CO - 0.1%
CO_2 - 0.9%
H_2O - 14.6%
SO_2 - 0.35 to 0.75%

The lime slurry circuit for the scrubber operates at approximately 2,500 gal/min flow rate. After the 5 percent solid lime slurry has been sprayed into the scrubber and contacted the gases, it leaves from the bottom at a pH of 6. The scrubber effluent is passed into a weir box to meter the flow. From the weir box, the slurry passes into the mixing tank which has an agitator and is used to control a pH to approximately 6.5 by lime addition at this point.

It has been found that the concentration of calcium hydroxide to pH relationship is nonlinear and is shown in the curve of Figure 5-9. The operator tries to maintain the system on the 6.5 to 7 pH plateau. If the pH goes beyond this, it tends to become overly sensitive to lime addition and can become as high as 10 very rapidly.

The lime is added to the mixing tank in a 14 percent slurry. This slurry is prepared elsewhere in the plant because the material is also used for another process. A 100 gal/min bleed is taken from the system on a continuous basis and is passed to the tailings impoundment dam.

It is estimated that recovery of water from the tailings pond is in the 30 to 40 percent range. Three to five percent of the total sulfur input is SO_3. Total particulate out of the stack, including both liquid and solid, is nominally 8 lb/hr.

The pressure drop across the scrubber will nominally be 13 inches of water but can go as high as 17-in of water. The main fan at the base of the stack pulls approximately 38 to 40-in

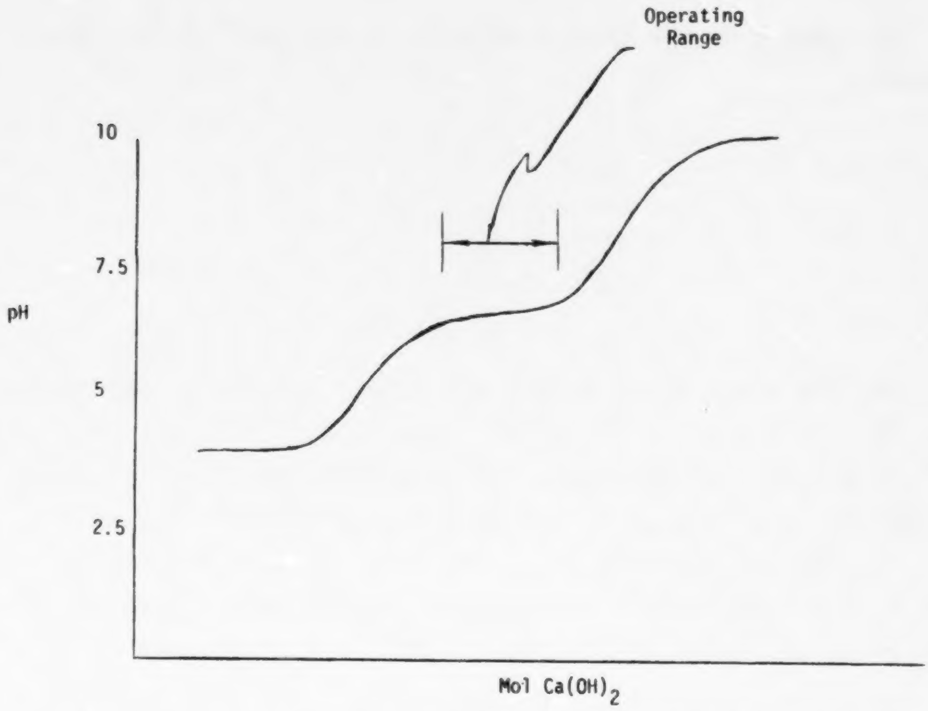


Figure 5-9. The pH Versus Calcium Hydroxide Concentration

of water. The Brinks mist eliminator produces approximately 7-in of water pressure drop.

The roaster is operated under negative pressure but very close to atmospheric. It is a relatively new roaster and is in very good condition. There is very little evidence of SO_2 in the roaster area when compared to roasters at some of the smelters in Arizona.

Considerable development work has been carried out to determine the loading of the balls within the scrubber. The original scrubber design is a UOP model TCA No. 500. This design has been modified by Duval. Presently, they use three stages of a 6 inch layer (static) of 7 gram balls. Screens are located between the layers, and the height between the screens is approximately 30-in.

The development work on the scrubber indicated that the balls must be floating or "teetering" in the gas stream in a position relatively in between the two screens. If the balls are operated too close to the upper screen, then blinding or blockage to flow occurs. If the balls are operated too low or close to the bottom screen, then the gas flow is again restricted.

5.3.5 SYSTEM OPERATION

It is necessary to shutdown the system a total of 6 hr/wk to enter the scrubbers and chip out the scale. This down-time falls within the State of Arizona regulations in terms of total SO_2 collected. Scrubber screens are generally replaced once every 6 months. Balls must be replaced every 3 to 5 months. Some cracking of the balls at the seams occurred; however, this has recently been corrected by a modified ball design.

Operation of the system is primarily controlled by pH of the slurry leaving the bottom of the scrubber. However, the quantity of the balls (which is adjusted by the static thickness of the ball layer) and the weight of the ball are also influencing factors. It is very easy for the system to become unstable from the pH standpoint and then the operation essentially goes out of control. As seen in the curve in Figure 5-9, if the pH is in the steeper portion of the curve the system tends to become critical from a control standpoint. Operation in the stable pH zone of four is not conducive to high scrubber efficiency. The best compromise has been found operating at a set point of about 6.5. Even at this set point there are wide swings of the pH, however, the system does stay in control since it has a time constant sufficient to shut off the lime once the pH begins to rise in time for the pH to return to a stabilized position. Fluctuations of the input SO_2 within the normal range do not seem to affect the system operation.

has a time constant sufficient to shut off the lime once the pH begins to rise in time for the pH to return to a stabilized position. Fluctuations of the input SO_2 within the normal range do not seem to affect the system operation.

5.3.6 APPLICATION OF DUVAL LIME SCRUBBING SYSTEM TO REVERBERATORY FURNACES

While the Duval Lime Scrubbing System is operating on metallurgical gases emitted from multihearth roasters, the problems are similar to reverberatories particularly since the SO_2 concentration is in the 0.3 to 0.75 percent concentration range. The gas temperature (entering the SO_2 system), particulate cleaning, and water content are the same or very similar. Since this system has been at satisfactory full-scale operation since 1973 it, at the very least, confirms the Japanese experience.

5.4 MAGNESIUM OXIDE SO_2 CONCENTRATION SYSTEM FOR REVERBERATORY FURNACE OFFGASES AT THE ONAHAMA COPPER SMELTER

5.4.1 HISTORY

The development and installation of the magnesium oxide SO_2 concentration system at the Onahama Smelter was performed as a joint effort between the Tsukishima Kikai Company (TSK) and Mitsubishi Metals Corporation. TSK is an independent organization devoted to engineering and construction of major industrial plants and equipment.

Development was started approximately 8 years ago in 1969 and required approximately 3 years to complete. The development phase consisted primarily of the 1/400 laboratory scale and then the 1/20th scale efforts. Most of this work took place at the Onahama Smelter.

The problems investigated during the development were the energy required, scaling, plugging, and the absopriton capacity. It was decided to use the magnesium oxide process to concentrate SO_2 from the reverberatory furnace offgas for direct acid plant processing at the time because in comparison to other processes, particularly the Wellman-Lord concentration system, the amount of energy used was a minimum. Also TSK considered that there was no feasible way to eliminate the sulfate formed when using the Wellman-Lord system.

The development effort used approximately six technical people for an equivalent period of 6 months over a total elapsed time of 3 years.

The initial order for the full-scale Onahama magnesium oxide system was given to TSK in the fall of 1972. Startup occurred in December 1972, and the shakedown phase was completed by May of 1973. Since 1973, well over 2 years of operating time has accrued.

5.4.2 MAGNESIUM OXIDE SYSTEM DESCRIPTION

Figure 5-10 is a flowsheet of the Onahama magnesium oxide system. The gases from the reverberatory furnace are treated with the same equipment as that used in the gypsum system using the initial washing tower and the secondary sea water cooled gas coolers (Section 5.2).

The gases pass from the absorber to a mist eliminator of the same design as that used for the gypsum system (Section 5.2). Following the mist eliminator, a fan with a suction pressure of 400 to 500 mm of water is located, followed by the electrostatic precipitator and then the stack. The offgases generally contain 20 ppm of SO_2 when they leave the stack.

The main absorbent circuit has three 75 kilowatt pumps and circulates the absorbent at approximately 1,200 m^3/hr. The overflow circuit from the bottom of the absorber takes the slurried magnesium sulfite through a 55 kilowatt pump to a liquid cyclone at a flow rate of approximately 200 m^3 per hour. The cyclone is used to rough-cut the slurry material to 40 to 50 percent solids.

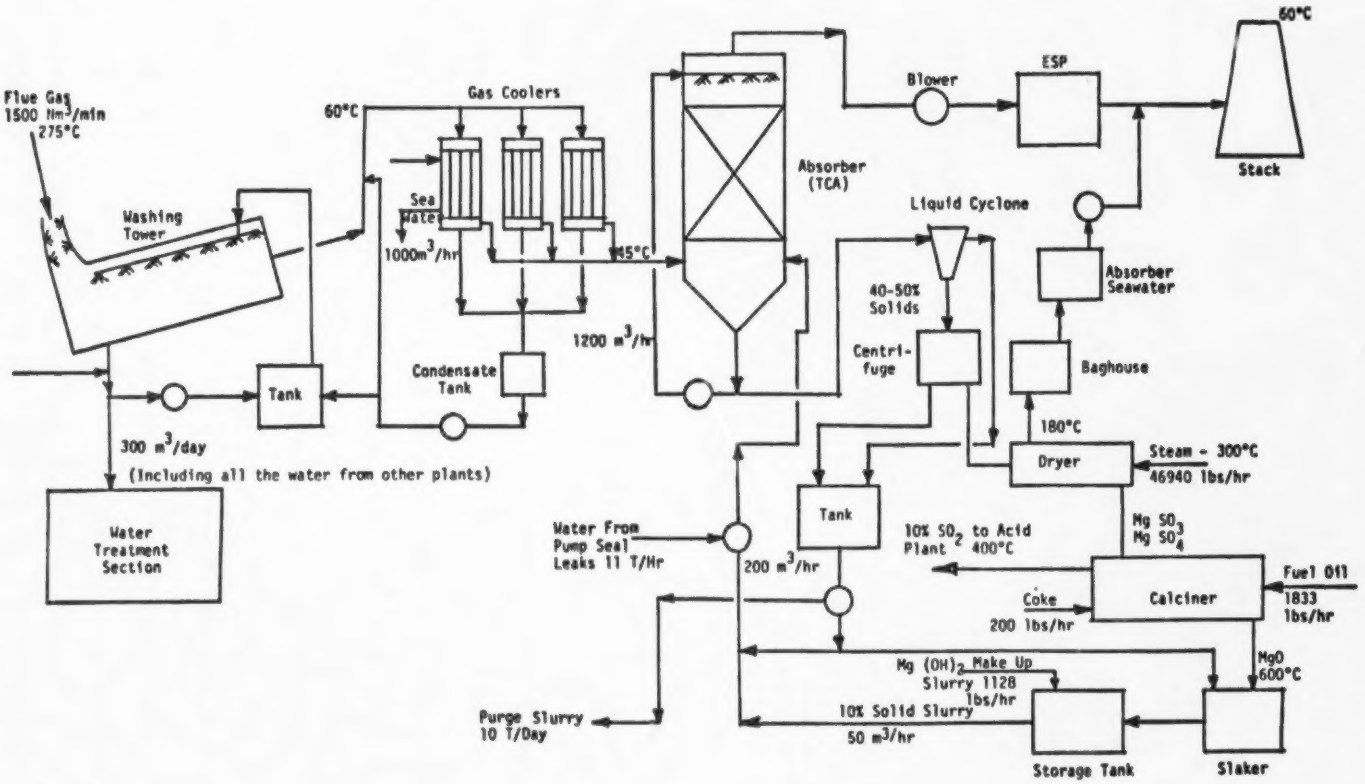

Flue Gas
1500 Nm3/min
275°C
Washing Tower
Tank
300 m3/day
(Including all the water from other plants)
Water Treatment Section
60°C
Gas Coolers
Sea Water
1000m3/hr
Condensate Tank
45°C
1200 m3/hr
Absorber (TCA)
Blower
ESP
Stack
60°C
Liquid Cyclone
40-50% Solids
Centri-fuge
Absorber Seawater
Baghouse
180°C
Dryer
Steam - 300°C
46940 lbs/hr
Tank
Water From Pump Seal Leaks 11 T/Hr
200 m3/hr
10% SO2 to Acid Plant 400°C
Mg SO3
Mg SO4
Calciner
Fuel Oil
1833 lbs/hr
Coke
200 lbs/hr
MgO
600°C
Mg (OH)2 Make Up Slurry 1128 lbs/hr
10% Solid Slurry
50 m3/hr
Purge Slurry 10 T/Day
Storage Tank
Slaker

Figure 5-10. Flow Sheet for MgO System at Onahama Smelter

The overflow from the cyclone goes downstream to the centrifuge centrate return system. The high solid content slurry cyclone underflow is then passed into 12 centrifuges for removing most of the remaining attached water. The centrate passes out of the centrifuge through a holding tank back to the absorber circuit.

The centrifuged material is passed by screw conveyor to a rotary dryer. The rotary dryer consists of a series of two pass single tubes through which steam at over 300°C is passed. These tubes do not recirculate the steam but allow it to condense and the condensate then flows back to the inlet end of the dryer and then out to waste. The gases in the dryer are at approximately 180°C and pass to the stack through a baghouse, an absorber, and an exhaust fan which operates at a minus 300 millimeters water suction pressure. The dried material passes from the dryer at 160°C to a screw conveyor where it is combined with coke through a variable speed rotary valve to pass into the rotary calciner.

The rotary calciner is fired with Bunker C oil and produces 800°C gas at the burner end. The calciner breaks down the magnesium sulfite to SO_2 and MgO, and passes a 10 percent SO_2 stream out to the acid plant at a temperature of approximately 400°C. In addition the magnesium sulfate is reduced by coke to magnesium sulfite. The magnesium oxide in the calciner flows out at 600°C to the slaker where it is mixed with the overflow from the centrifuge and cyclone systems. The magnesium oxide is converted to magnesium hydroxide in the slaker and the slurry is then passed to the magnesium hydroxide storage tank. This tank also receives new magnesium hydroxide.

The amount of makeup dry magnesium hydroxide added is 0.08 kg/kg of input SO_2. The makeup slurry at 10 percent solids is pumped back to the absorber at a rate of approximately 50 m^3/hr.

Component design and cost considerations are briefly discussed in Appendix O.

5.4.3 OPERATING CONDITIONS

5.4.3.1 Input Material and Preparation

The magnesium hydroxide is purchased as a liquid containing 20 to 30 percent solids of $Mg(OH)_2$. Analysis of this material is:

● CaO	0.97 percent
● SO_4	0.30 percent
● M_gO	17.68 percent
● H_2O	remainder

The specific gravity of the absorption slurry is 1.1 to 1.2. The turnover ratio of the makeup magnesium hydroxide is approximately 20 times.

The magnesium hydroxide is obtained from seabrine. There are no special purifying requirements, and the material is produced in a plant nearby. There is no major change in the reactivity of the magnesium hydroxide during use perhaps because it is replaced once every 20 cycles. The amount of makeup dry magnesium hydroxide that is added is 0.08 kilograms per kilogram of input SO_2.

A total of 3.5 metric tons of steam are used in the dryer per metric ton of sulfur dioxide.

The amount of coke that is used is 0.012 kg/kg of sulfur dioxide. The only function of the coke is to reduce the magnesium sulfate in the calciner. The sizing of the coke is not critical, however, it cannot be too large because it would not all take part in the reaction and it cannot be too small because of the resulting dust problem.

Bunker C fuel oil is used in the calciner at the rate of 1,833 lb/hr or 0.13 lb/hr SO_2.

Pump seal leakage water into the system is approximately 11 ton/hr.

5.4.3.2 Internal Operating Conditions

Chemical reactions are discussed in Appendix P.

A separate crystallization step is not required because crystals are formed in the absorber. Crystal size and uniformity are not a problem because only the magnesium sulfite hexahydrate is formed. There is no evidence of the trihydrate being formed.

Crystal size, while influencing caking, is not changed or adjusted. The crystals that are picked up in the centrate from the centrifuge do not affect the process since the centrate is returned to the absorber.

The L/G ratio in the absorber is 13 to 14. The absorbent and regeneration subsystem pH controls are important, and are considered proprietary.

The system appears to have considerable capability for absorbing fluctuations in the SO_2 from the reverberatory furnace. This is inherent because of the capacity of the absorbent, the supply of the absorbent, and the fact that the pH is maintained constant. Thus, when a peak SO_2 arrives, additional magnesium hydroxide increases the absorbent capability of the system. Makeup magnesium hydroxide is 0.08 kg/kg of inlet sulfur dioxide and includes reheat and other losses. Below a pH of 6, magnesium bisulfite begins to form and must be bled from the system, because it is not regenerable.

There are no problems with magnesium sulfate buildup. The turnover ratio and makeup material are sufficient to eliminate this problem. Coke is reprocessed from the calciner and recycled.

5.4.3.3 Output

An average 10 percent sulfur dioxide gas stream is generated by the calcine. This may reach a high value of 13 percent SO_2.

The gas leaving the dryer passes through a bag filter, through a sea water scrubber, and then to the stack. Water from this scrubber is discharged to the ocean.

Some excess water is purged to the settling pit and then to the ocean at the rate of 10 ton/day.

5.4.3.4 Maintenance and Operation

Every month the absorption tower is changed. A spare tower is included in this system. Each tower is cleaned with an acid wash for 1 day and left as a spare for 1 month until the second tower is taken out of line. It is only in the absorption tower that any indication of plugging occurs. There are no other cleaning problems.

Ball wear in the TCA absorber is controlled by replacement every 2 to 3 months.

Loss of absorbent has been as high as 10 percent of the MgO feed and occurs in the acid plant wash towers since the wash water is discharged to the ocean.

The MgO is slaked adequately without heating but it has been necessary to do some grinding of the larger agglomerates.

5.4.3.5 Area Required

The area required for the 55,000 scfm magnesium hydroxide plant at the Onahama Smelter is 5,500 m^2.

5.4.4 APPLICATION OF THE MAGNESIUM OXIDE SO_2 CONTROL SYSTEM TO U.S. SMELTERS

Considerable work on MgO systems has been done by U.S. contractors. A pilot system was installed at the Boston Edison Power Plant (Mystic Power Generating Station) and at Potomic Electric. These latter encountered experimental difficulties and are not now in operation, but the experience obtained was sufficiently promising to convince Philadelphia Electric to install a system. This is currently in operation and several more are under construction for this company. Design and construction is by United Engineers who are also designing a system for the TVA Johnsville Station in Tennessee.

While there does not appear to be a single outstanding reason for the early difficulties encountered, it can generally be said that development and operating experience in Japan was greater than in the U.S. at the time the first systems were installed. This is somewhat confirmed by the fact that the U.S. company, CHEMICO, which took part in early system development, also installed their third magnesium oxide installation at the Chiba refinery in Japan and this system is apparently working satisfactorily. While it uses the Claus process for converting the concentrated SO_2 to sulfur, the first part of this system is essentially the same with the modified design technology to improve system operations and operating time.

One of the major differences between the U.S. and the Japanese systems is that the U.S. used a venturi scrubber while the Japanese used a TCA scrubber. However, in discussing this with the Japanese, they do not feel this is a major difference and in fact have indicated that they would be interested in using a venturi scrubber. The Japanese use two alternate scrubbers instead of one, and this could be a major factor in maintaining on-stream time.

Other factors such as differences in pH throughout the system and minor path variation could make the difference in achieving a successfully operating system.

Replacing of the MgO at relatively frequent intervals could aid in operation of this system. The purchase of the MgO in the form of a magnesium hydroxide slurry by the Japanese apparently facilitated the handling of this material compared to the mixing problems that were encountered in the U.S. The fact that recycled MgO slurry apparently was more satisfactory from an SO_2 removal standpoint than was the virgin MgO in the U.S. experience further supports this contention.

Except for the potential problem of water supply, it appears that there is no major reason why the MgO system cannot be used as an SO_2 concentration system for the reverberatory furnace offgas.

The MgO system at the Onahama smelter uses the following material:

MgO	12.5 lb/min
Bunker C fuel oil	30.6 lb/min
Coke	3.1 lb/min
Steam	812 lb/min

Calculation if the water and material balances for the MgO system at Onahama based on a design inlets gas flow of 1,500 Nm^3/min are shown in Appendix Q. A summary of the water balance follows:

Water in flue gas	445 lb/min
Water in gas at outlet of washing tower	585 lb/min
Water added to flue gas in washing tower	140 lb/min
Water in gas at outlet of gas coolers	250 lb/min
Total water removed from flue gas in combined washing tower and gas cooler	195 lb/min
Water makeup for gas cooler section	140 lb/min
Water in MgO makeup slurry	59 lb/min
Water of crystalization in $MgSO_3 \cdot 6H_2O$	392 lb/min
Water adhered to crystals	378 lb/min
Water lost in dryer	478 lb/min
Water in pump seals	411 lb/min
Water purged in slurry	16 lb/min
Water into MgO system (445 + 140 + 59 + 411)	1,055 lb/min
Water out of MgO system (195 + 392 + 478 + 16)	1,081 lb/min

With a system designed for minimum water use by recycling from the water treatment plant the following projected water balance is estimated for 1,500 Nm^3/mm of gas at 2.6 percent SO_2.

Water in flue gas, W_f	444 lb/min
Water leaving stack, W_s	242 lb/min
Water condensed from flue gas, W_{fg}	202 lb/min
Water to water treatment section from washing tower and gas cooler	202 lb/min

• Water lost in gas cooling sections, W_{ge} (10% purge, 20% evaporation of feed to water treatment)	61 lb/min
• Makeup water in MgO slurry, W_{mg}	59 lb/min
• Water of crystalization and surface moisture driven off in dryer, W_c	478 lb/min
• Slurry purge water, W_{sp}	14 lb/min

5.5 CITRATE PROCESSES

5.5.1 GENERAL

The two major developers of SO_2 concentration systems based on citrate type absorbents are the U.S. Bureau of Mines in Salt Lake City and Flakt-Boliden in Sweden. Each group has conducted pilot plant tests using metallurgical plant gases.

The Bureau of Mines process was developed as a result of investigations showing that organic acids such as acetic, citric, lactic, and similar acids had a great affinity for SO_2.[82] A mixture of citric acid, sodium citrate, and sodium thiosulfate was selected for further development because of its chemical stability, low vapor pressure, and adequate pH buffering capacity. This system was designed to produce sulfur by using manufactured H_2S as a reducing agent. Pilot tests on gases from a copper smelter reverberatory furnace encountered experimental difficulties but indicate the potential at least for the absorption of SO_2 from these gases into the citrate solution.

In recent years, efforts to develop a commercial desulfurization process resulted in a cooperative program between Boliden Aktiebolag and Flakt (Svenska Flaktfabrikan). The Flakt-Boliden system resulted from long range development work carried out by several copper smelters and technical institutes in Scandinavia. The work developed from a successful SO_2 control system using only low temperature water as absorbent, which has been in operation at the Boliden AB Ronnskarverken Smelter in Skelleftehamn, Sweden since 1970. The absorbent which was developed was a brine of citric acid and sodium citrate which improved the flexibility of the system over straight cold water. The exact composition of the absorbent depends on a number of parameters such as SO_2 concentration in the feed, gas temperature and required SO_2 concentration and absorbent temperature.

Both groups have developed similar systems that have, on a pilot plant level, indicated the potential for absorption of the lean SO_2 stream from the copper smelter reverberatory furnace to concentrate SO_2 at absorption efficiencies well over 95 percent. The Bureau of Mines encountered considerable development problems in the portion of the system downstream of the absorption section in the H_2S producing and sulfur reduction sections. Flakt-Boliden considers their system simply a concentration technique that generates concentrated SO_2 that can then be used to produce liquid SO_2, H_2SO_4, or S depending upon the specific application. The success of both groups with the absorption system indicates that, for reverberatory furnace applications, the citrate system can be used to upgrade the SO_2 concentration to allow additional processing to either liquid SO_2, sulfuric acid, or sulfur through a coal reduction system. The use of the H_2S reduction approach has not been satisfactorily demonstrated as an integrated system.

5.5.2 BUREAU OF MINES CITRATE PROCESS

5.5.2.1 Introduction and History

The Bureau of Mines Salt Lake City Metallurgy Research Center started research on flue gas desulfurization with particular emphasis on control of SO_2 emissions from the nonferrous smelting industry. Absorption in an aqueous solution of citric acid and sodium citrate was selected due to good chemical stability, low vapor pressure, and adequate pH buffering capacity. The purity and physical character of the resulting precipitated sulfur was also considered advantageous.

After successful laboratory results, the Bureau of Mines in 1970, constructed and operated a pilot plant to remove SO_2 from flue gas from a copper reverberatory furnace. It was a joint venture between the Bureau of Mines and Magma Copper Company. This plant, located at San Manuel Smelter in Arizona, treated 300 scfm of gas containing 1.0 to 1.5 percent SO_2 and consistently removed 93 to 99 percent of SO_2.[83] Failures of the gas cleaning system, pump breakdowns, and plugging of flow lines with precipitates and melted sulfur, occurred during the testing. Most of the problems occurred in the SO_2 to sulfur conversion circuit. Useful data on consumption of citric acid and other reagents were not obtained, but the SO_2 absorption and regeneration system proved manageable for removal of 93 to 99 percent of the SO_2 from the smelter gas.

Two other pilot plant investigations were undertaken to obtain data for engineering evaluation and cost estimates. One pilot plant was independently built and operated by Arthur G. McKee and Company, Peabody Engineering Systems, and Pfizer, Inc., at Terre Haute, Indiana in 1972. This pilot plant treated stack gases from a coal-fired steam-generating station. After several modifications to arrive at a final equipment configuration, the pilot plant operated from March 15 to September 1, 1974, logging 2,300 operating hours. The longest sustained run was 180 hours. The pilot plant treated 2,000 scfm flue gas containing 0.1 to 0.2 percent SO_2 and consistently removed 95 to 97 percent of SO_2. Equipment difficulties were also encountered, thus preventing complete steady-state operation of the entire system.

The other pilot plant was constructed by the Bureau of Mines and operated jointly by the Bureau of Mines and the Bunker Hill Company at the lead smelter in Kellogg, Idaho. Nominal capacity of the Kellogg pilot plant was 1,000 scfm of 0.5 percent SO_2 gas, taken as a slipstream from a Lurgi updraft lead sintering machine yielding about 1/3 ton of sulfur per day.[84] Here, again, difficulties with the SO_2 reduction system, as well as problems with maintaining a steady-state feed stream, prevented conclusive system tests.

5.5.2.2 Process Description

The generalized flow diagram for the Bureau of Mines citrate process is given in Figure 5-11. Process chemistry is discussed in Appendix R. Incoming gases are cleaned of particulate matter and acid mist and cooled to 115° to 150°F. This is done in a combination of a baghouse, packed scrubber, and electrostatic mist precipitator, or a venturi scrubber.

The cooled and cleaned gas is then led to an absorber. The absorber is a countercurrent packed scrubber with a liquid to gas flow of nearly 10 gal/1,000 ft^3. The liquid is an aqueous solution of sodium citrate and citric acid. The cleaned gas from the absorber is exhausted to the atmosphere through a stack.

The SO_2 rich citrate solution from the bottom of the absorber is fed by a level control to a continuous stirred tank reactor system countercurrent to a flow of H_2S gas. In the reactor, the SO_2 is reduced to sulfur, and the citrate solution is regenerated. Sulfur slurry from the reactor is fed to the sulfur separation system. In the sulfur separation unit, sulfur is removed by oil flotation. The floated sulfur at 35 to 45 percent solid is fed through a heater to raise the temperature above 125°C to melt the sulfur. Liquid phases are separated in a decanter under a pressure of 35 psi, the bottom layer is drawn off as high-quality molten yellow sulfur, and the citrate solution top layer, at reduced pressure, is discharged to a flash drum.

Citrate solution from the decanter can be bypassed around or into a vacuum crystallizer where sodium sulfate is removed from the solution by cooling to a temperature well above the freezing point of water.

The H_2S gas for the regenerator is made from the recovered sulfur in the H_2S reactor. Filtered liquid sulfur is preheated

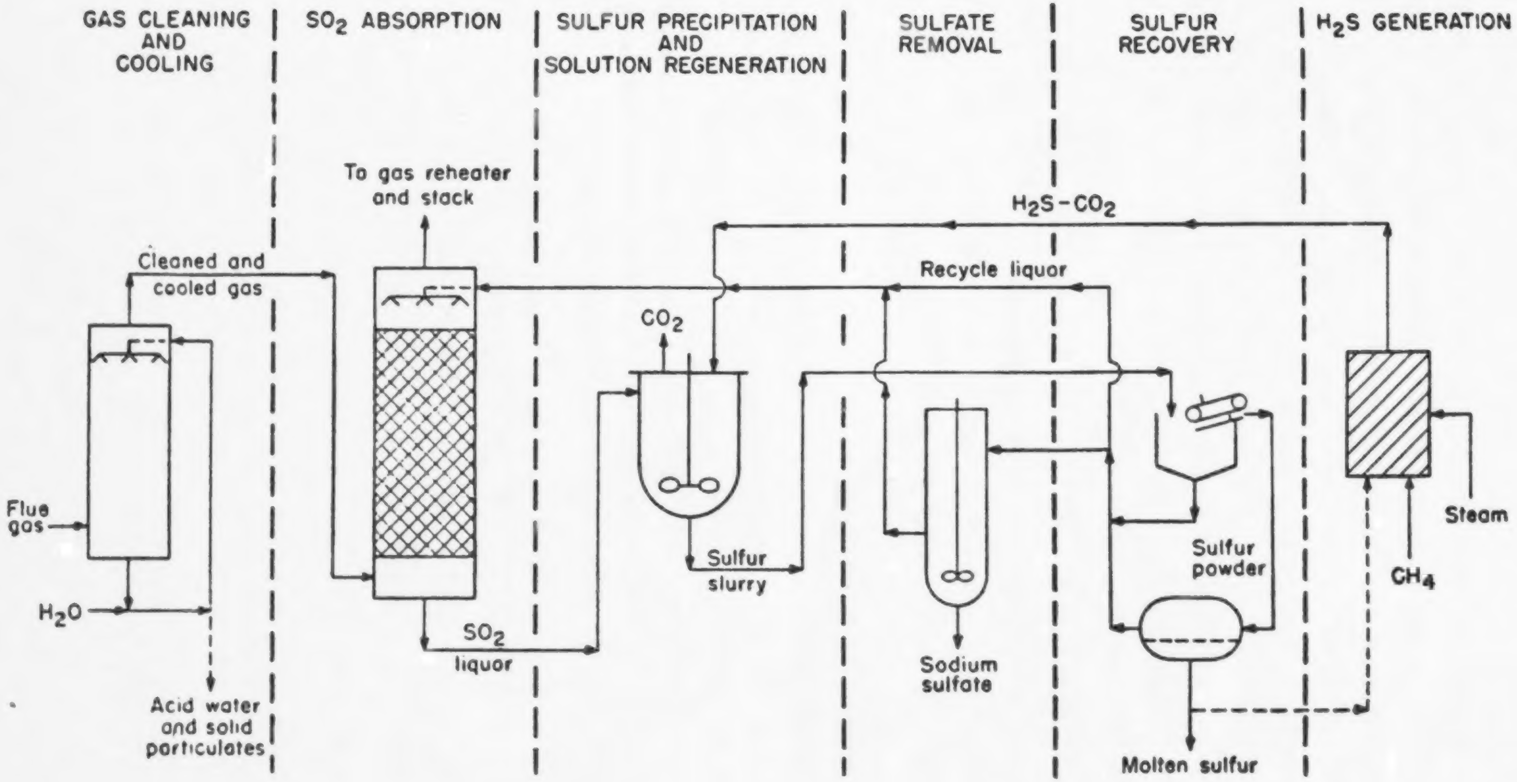

GAS CLEANING AND COOLING
SO_2 ABSORPTION
SULFUR PRECIPITATION AND SOLUTION REGENERATION
SULFATE REMOVAL
SULFUR RECOVERY
H_2S GENERATION
To gas reheater and stack
H_2S-CO_2
Cleaned and cooled gas
Recycle liquor
CO_2
Flue gas
H_2O
Acid water and solid particulates
SO_2 liquor
Sulfur slurry
Sodium sulfate
Sulfur powder
Molten sulfur
Steam
CH_4

Figure 5-11. Flow Diagram for the Bureau of Mines Citrate Process

by the H_2S reactor effluent to 785°F. It is then vaporized in a heater at 1.050 °F and superheater to 1,200°F. Part of the steam and the natural gas required for H_2S generation are preheated to 1,050°F and mixed with a portion of the sulfur vapor. The mixed gas at 1,168°F enters the top of a quench-cooled catalytic H_2S reactor. The remaining sulfur vapor is blended with unpreheated steam-natural gas mixture and is injected into the catalytic bed to maintain near isothermal bed temperature. The reaction is exothermic and the effluent from the reactor leaves at 1,292°F.

The hot gas from the H_2S reactor preheats the sulfur feed to the reactor, and it is then used to generate steam required for H_2S generation. The gas is cooled to 140°F and is then fed to the citrate absorbent regenerator.

5.5.2.3 Problems With the Process

The Bureau of Mines citrate process has a high absorption efficiency and can be used within a wide range of SO_2 corcentrations. It produces elemental sulfur which is very desirable from the marketing point of view. But there are a few problems associated with the process that appeared during the several demonstration test programs. These problems are enumerated herein:

1. The process is relatively complex and therefore the reliability of the process is not yet very good.
2. The process uses natural gas for producing H_2S. With the future supplies of natural gas in doubt, its usage is not very desirable.
3. Nearly 2 to 3 percent of incoming SO_2 is oxidized.
4. Kerosene consumption is nearly 85 lb per net long ton of sulfur produced, even though the Bureau of Mines reports that it may be possible to recover 75 percent of this amount.[86]
5. Additional development effort is required for the H_2S generating system and the sulfur handling system.

The Bureau of Mines is, however, looking into steam stripping of the pregnant absorbent solution as an alternative to sulfur precipitation by H_2S to produce strong SO_2 gas for feed to a sulfuric acid plant. This alternative would simplify the process significantly and would probably eliminate most of the aforementioned problems.

5.5.3 FLAKT-BOLIDEN CITRATE PROCESS

5.5.3.1 Introduction and History

Boliden AB Ronnskarsverken Smelter at Skelleftehamn, Sweden has been removing sulfur dioxide from smelter gases by absorption in cold water at full scale since 1970 (see Figure 5-12). The flue gases treate are a blend of gases from multiple hearth furnaces, two electric furnace converters, and a lead smelter. The volume flow of gases is in the range of 60,000 to 70,000 m^3/hr at 300°F, containing SO_2 concentrations from 0.5 percent with a 3 percent average. The absorbed sulfur dioxide is stripped by heating with steam. The plant produces 6 ton/hr of liquid SO_2.[87]

During December 1976, a new plant (Figure 5-13) for liquid SO_2 production was put into operation at the aforementioned smelter. The maximum production rate of liquid SO_2 is 16 ton/hr, of which most will be sold to the Swedish pulp industry.[88] However, to give flexibility, the liquid SO_2 can also be evaporated and fed to one of the existing sulfuric acid plants in order to keep the SO_2 content of the feed gas to the acid plant approximately constant.

Absorption of SO_2 in cold water at this smelter is possible by the ample supply of cold water (5°C to 8°C) during the entire year.[89] In situations where cold water is not available year-round, it is desirable to improve the SO_2 absorption properties of water. This process is a result of long range development work carried out by the Boliden Company of Sweden, the Norwegian Technical Institute SINTEF, and FLAKT (Svenska Flaktfabriken). It was found

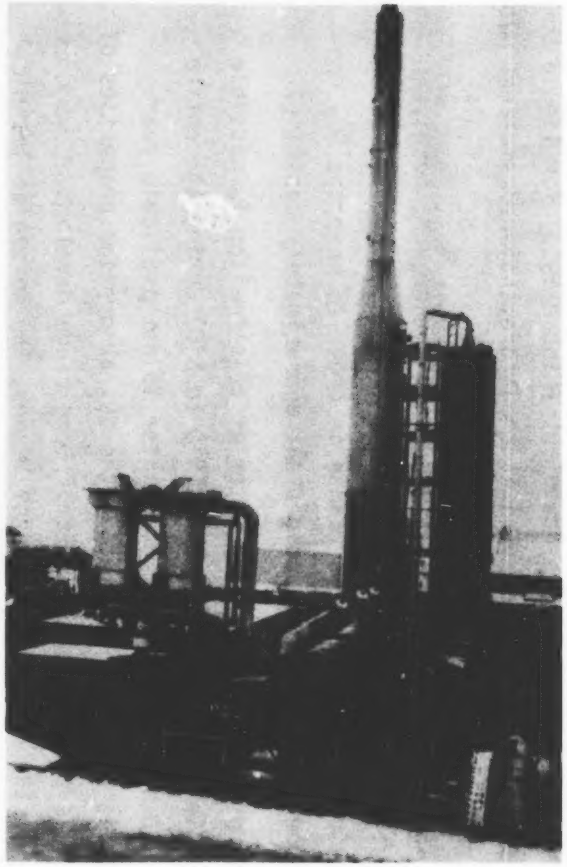


Figure 5-12. THE SO_2-I PLANT AT THE RÖNNSKÄR, SMELTER, SWEDEN OPERATING SINCE 1970. Cold water is used as absorbent and production is 6 ton/h of liquid SO_2.

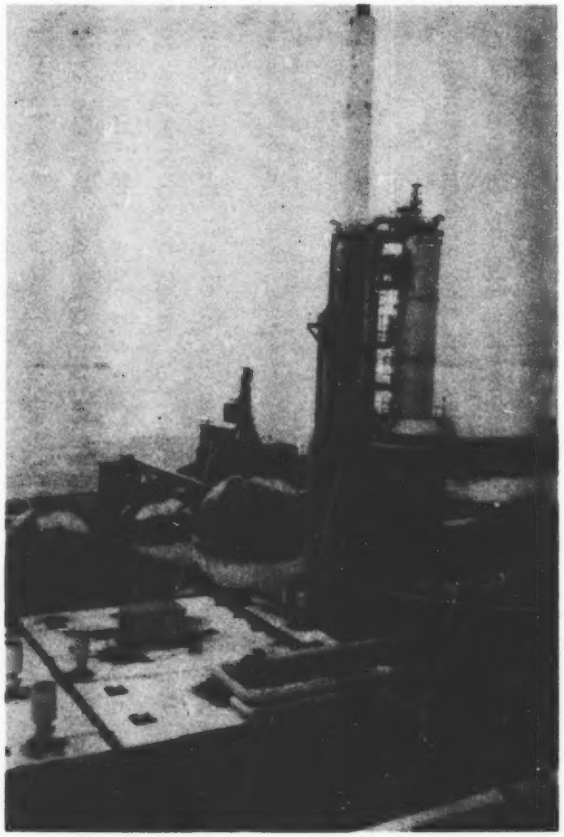


Figure 5-13. THE SO_2-II PLANT AT THE RÖNNSKÄR, SWEDEN, SMELTER OPERATING SINCE LATE 1976. Same absorbent as used for the SO_2-I plant but production is 16 ton/h liquid SO_2.

that by adding weak bases which have good buffering properties to water, the SO_2 absorption capacity is increased.

The base chosen for this purpose was a combination of citric acid and sodium hydroxide. Citric acid has a very low vapor pressure and shows great chemical stability. In recent years, development work on a commercial desulfurization system, based on citrate as absorbent, has been conducted as a cooperative venture between Boliden Aktiebolog and FLAKT.

The Flakt-Boliden citrate process is based on an absorption stripping technique in which the absorbent is a brine of citric acid and sodium citrate. The pregnant absorbent goes to a stripper where a mixture of sulfur dioxide and water vapor is driven off. After condensing the main quantity of water, the sulfur dioxide may be put to use in different ways depending on the local market requirements. A gas mixture, containing some water vapor, can for instance be used directly in a Claus plant for production of elemental sulfur or in a contact plant for production of sulfuric acid. The citrate process may be used for gases with varying concentration of SO_2, such as tail gases from metallurgical and chemical processes as well as from power plant flue gases. Since the absorbent is a solution rather than a slurry, scaling and plugging of equipment is minimized.

5.5.3.2 Process Description

The schematic of the Flakt-Boliden citrate process is given in Figure 5-14. Process chemistry is described in Appendix S. The incoming gas (prior to going to the absorption tower) is cleaned in a high-efficiency particulate collector, preferably an electrostatic precipitator, and then cooled to saturation by direct water injection. In addition to dust, sulfuric acid mist is removed in a mist precipitator before the absorption step to minimize sodium sulfate formation in the absorber which would increase the purge requirements. The important process variables at the absorption step are:

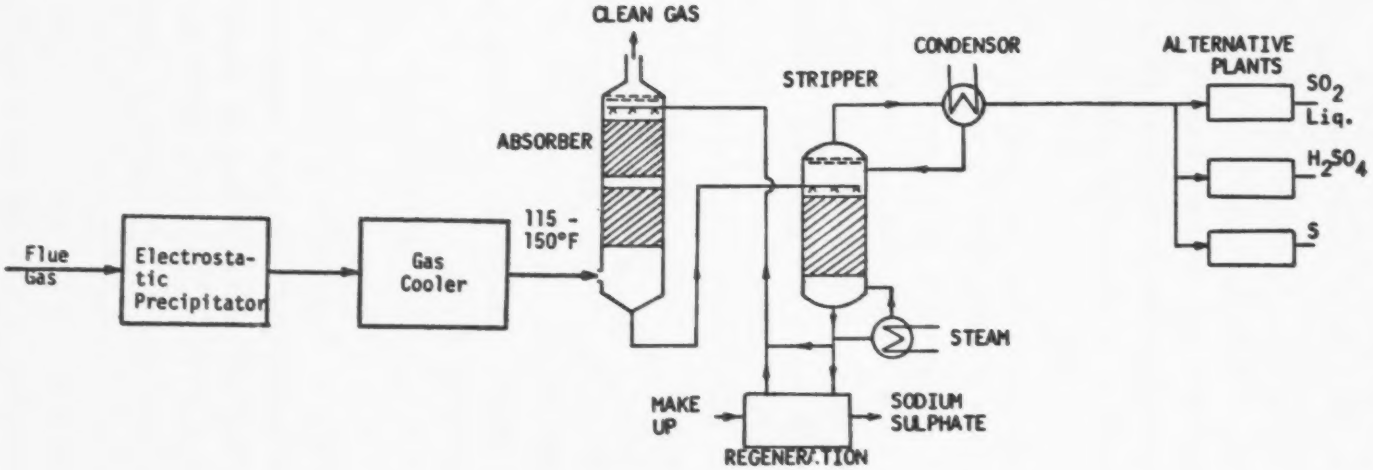

CLEAN GAS
CONDENSOR
ALTERNATIVE PLANTS
STRIPPER
SO_2 Liq.
ABSORBER
H_2SO_4
115 - 150°F
S
Flue Gas
Electrostatic Precipitator
Gas Cooler
STEAM
MAKE UP
SODIUM SULPHATE
REGENERATION

Figure 5-14. Flow Diagram for the Flakt-Boliden Citrate Process

1. Liquid-to-gas flow ratio in the absorber
2. Sulfur dioxide content of the incoming gas
3. Composition of the solution
4. Temperature of operation

The gas temperature at the inlet to the absorber is in the range of 115° to 150°F.[90] The cooled and saturated gas containing SO_2 is fed into the bottom of an absorption tower, where it meets the absorbent in counterflow. The composition of the absorbent depends on a number of parameters such as incoming SO_2 concentration, gas temperature, and required absorption efficiency. The absorption of SO_2 takes place under atmospheric pressure and close to equilibrium between the SO_2 concentration in the gas and that in the solution. The absorption of SO_2 takes place at isothermal conditions. The absorption efficiency is in the range of 95 to 99 percent. The cleaned gas after passing through a demister is passed to the atmosphere through a stack.

The SO_2 laden solution is pumped from the bottom of the absorption tower to the top of the stripping tower. The stripping is accomplished by steam treatment in countercontact to the liquid flow. As the vapor pressure of water increases more rapidly than that of SO_2, it is favorable to strip at reduced pressure (down to approximately one-tenth atmosphere). At the bottom of the stripping tower, low pressure steam is introduced and the tower is kept under vacuum producing a mixture of SO_2 and water vapor. From the bottom of the stripping tower, the absorbent, now with just a small fraction of SO_2, is recirculated to the absorber. The fact that the stripping takes place under vacuum affects steam consumption favorably and low-pressure steam or even hot water can be used.

The steam consumption in the stripper is directly related to the SO_2 concentration in the flue gas. The higher the SO_2 concentration, the lower the specific steam consumption. For example, with 3 percent SO_2 in the flue gas, the steam consumption is roughly 2 ton/ton of SO_2 stripped. For 2 percent SO_2 in the flue gas, the steam consumption increases to 3 ton/ton of SO_2 stripped. And for 1 percent SO_2 in the flue gas, the steam consumption is further increased to 6 ton/ton of SO_2 stripped.[91]

The steam consumption in the stripper is also related to the stripping temperature.[92] The steam consumption increases with an increase in the stripping temperature, especially when the flue gases with low SO_2 concentration are being treated. So it is highly desirable to operate the stripper at the lowest possible temperature. It should, however, be pointed out that the low pressure steam required can be available as a waste product from smelter operations.

The mixture of SO_2 and water from the stripping column is cooled in a condenser where most of the water is separated. The condensate, containing only a small quantity of SO_2, is returned to the stripping column.

The concentrated SO_2 gas which can be as high as 95 percent with a water saturation temperature of 30°C can be conveyed directly to a Claus plant for the production of elemental sulfur, a contact plant for sulfuric acid production, or condensed by refrigeration to liquid SO_2.

In the case of liquid SO_2 production, the water remaining in the gas is removed by contact with concentrated sulfuric acid in a small packed tower. After drying, the SO_2 gas still contains a small amount of inert gas. The dried SO_2 gas is conveyed to a Freon cooler where it is condensed into liquid SO_2. The liquid is pumped into a storage tank kept under pressure. The tail gas is returned to the absorber.

The main impurity accumulated in the closed absorption loop is sodium sulfate. Different concentrations of SO_3 in the in-going gas are encountered as well as some oxidation of SO_2 in the absorption tower. One advantage of the citrate absorbent is that the oxidation of sulfite to sulfate is inhibited by the citrate, mainly due to the complex-binding character of the citrate ion which prevents heavy metal ions from acting as oxidation catalyst. Flakt has also developed information on the effects of trace metals which would promote oxidation.

Even if the amount of sulfate formed in the sodium citrate solution is small, it must be removed when the sulfate content has reached a certain level. This can be attained by an intermittent or or continuous bleed-off from the stripper of approximately 1 percent of the stripped solution, for regeneration in a special regenerating step. During regeneration, the sodium citrate and sodium sulfate are separated from the solution. This is done by using seed crystals and a cooling unit to recover sodium citrate and remove sodium sulfate. Details of this regeneration system are presented in U.S. Patent No. 3,886,069.[93] The solution is returned to the absorbent. The sodium sulfate is a waste product.

A pilot plant, Figure 5-15, was used to conduct tests with the citrate absorbent. The main purpose of the tests was to establish a design background to the absorption/stripping process and to investigate the influences of different components in the raw gas on the oxidation of SO_2 in the absorbent.

The pilot plant absorber and stripper are conventionally packed towers with highly efficient packing, providing good mass transfer characteristics and countercurrent flow of gas and liquid. The pilot plant is connected to the inlet of one of the sulfuric acid plants at Ronnskar and receives part of this feed gas which was cooled and cleaned of particulate matter.

The raw gas originates from different metallurgical operations in the copper and lead smelters. As these processes are not continuous, the SO_2 concentration fluctuates.[95] The SO_2 concentration varies between 0.2 and 6.0 percent by volume, but is mostly constant at one level for sufficient time to make several measurements possible of steady-state conditions. Thus, the pilot plant test results give information about the influence of different parameters on a wide range of SO_2 concentrations. Inlet and outlet SO_2 concentrations are both continuously measured with IR instruments.

Figure 5-15. Flakt-Boliden Pilot Plant at Ronnskar Smelter, Sweden.

The liquid-to-gas ratio in the absorber can be varied approximately between 1 and 4-ℓ/m^3. And the stripping can be performed under varying pressures, from approximately 0.1 atmosphere absolute pressure to atmospheric pressure.[96]

Flakt reports that the test results look very promising. The oxidation rates were found to be very low with an average value of about 0.1 percent of absorbed SO_2. This oxidation rate is at least an order of magnitude lower than found in the concentrated sodium sulfite/hydrogen sulfite process. Consequently, the demand for make up of chemicals should be very low in the Flakt-Boliden process.

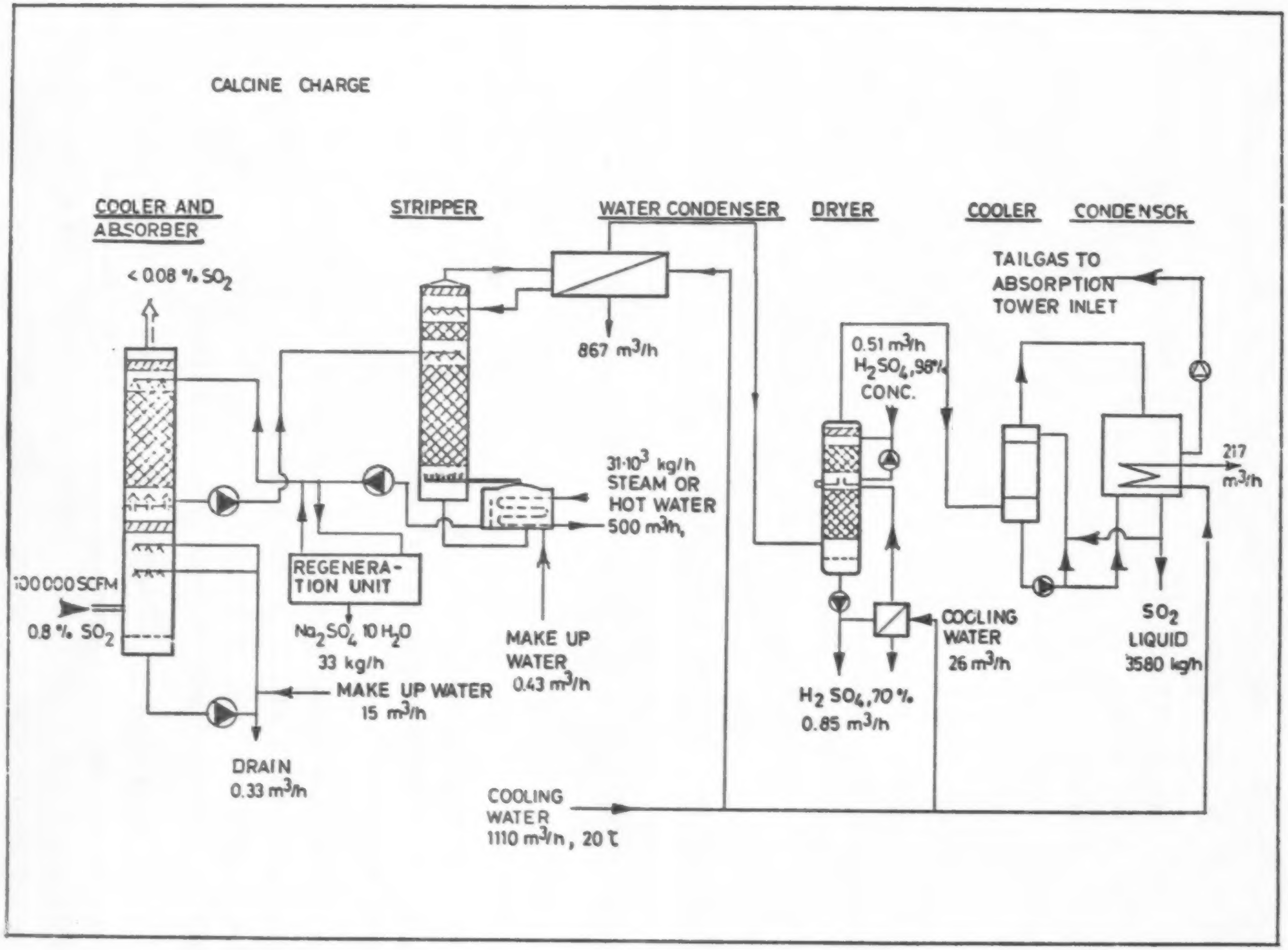
The specific steam consumption in the stripper increased, with a decrease of SO_2 concentration in the feed gas. However, according to Flakt, a new process development indicates significant decrease in the steam consumption, especially at low SO_2 concentrations in the feed gas.[97] No details of this new process were available at the time of writing this report.

5.5.3.3 Example of Green and Calcine Charge Reverberatory Furnace SO_2 Control Systems

A typical Flakt-Boliden SO_2 recovery process for green and calcine charge is shown in Figures 5-16 and 5-17. These flow sheets include material balance for a 100,000 scfm system with 0.8 percent SO_2 for the calcine charge and 1.5 percent SO_2 for the green charge examples.[98]

The process shown assumes that the regenerated SO_2 will be liquified as the product. If the gases are to be used to produce sulfuric acid, the H_2SO_4 dryer and the SO_2 liquefaction system would be eliminated and replaced by the acid plant system.

The SO_2 gas generated by the concentration system is 1,220 Nm^3/hr for the calcine charge and 2,300 Nm^3/hr for the green charge with a water saturation temperature of 30°C. The system was designed for removing 90 percent of the SO_2 in the gases. Summary data are shown in Table 5-1.



CALCINE CHARGE
COOLER AND ABSORBER
STRIPPER
WATER CONDENSER
DRYER
COOLER
CONDENSOR
< 0.08 % SO2
100 000 SCFM
0.8 % SO2
867 m3/h
REGENERATION UNIT
Na2SO4 10 H2O
33 kg/h
MAKE UP WATER
15 m3/h
DRAIN
0.33 m3/h
31·10³ kg/h
STEAM OR
HOT WATER
500 m3/h
MAKE UP WATER
0.43 m3/h
COOLING WATER
1110 m3/h, 20 ℃
0.51 m3/h
H2SO4, 98%
CONC.
H2 SO4, 70 %
0.85 m3/h
COOLING WATER
26 m3/h
TAILGAS TO ABSORPTION TOWER INLET
217 m3/h
SO2
LIQUID
3580 kg/h

Figure 5-16. Calcine Charge Reverberatory Furnace Offgas Flakt Citrate SO_2 Control System

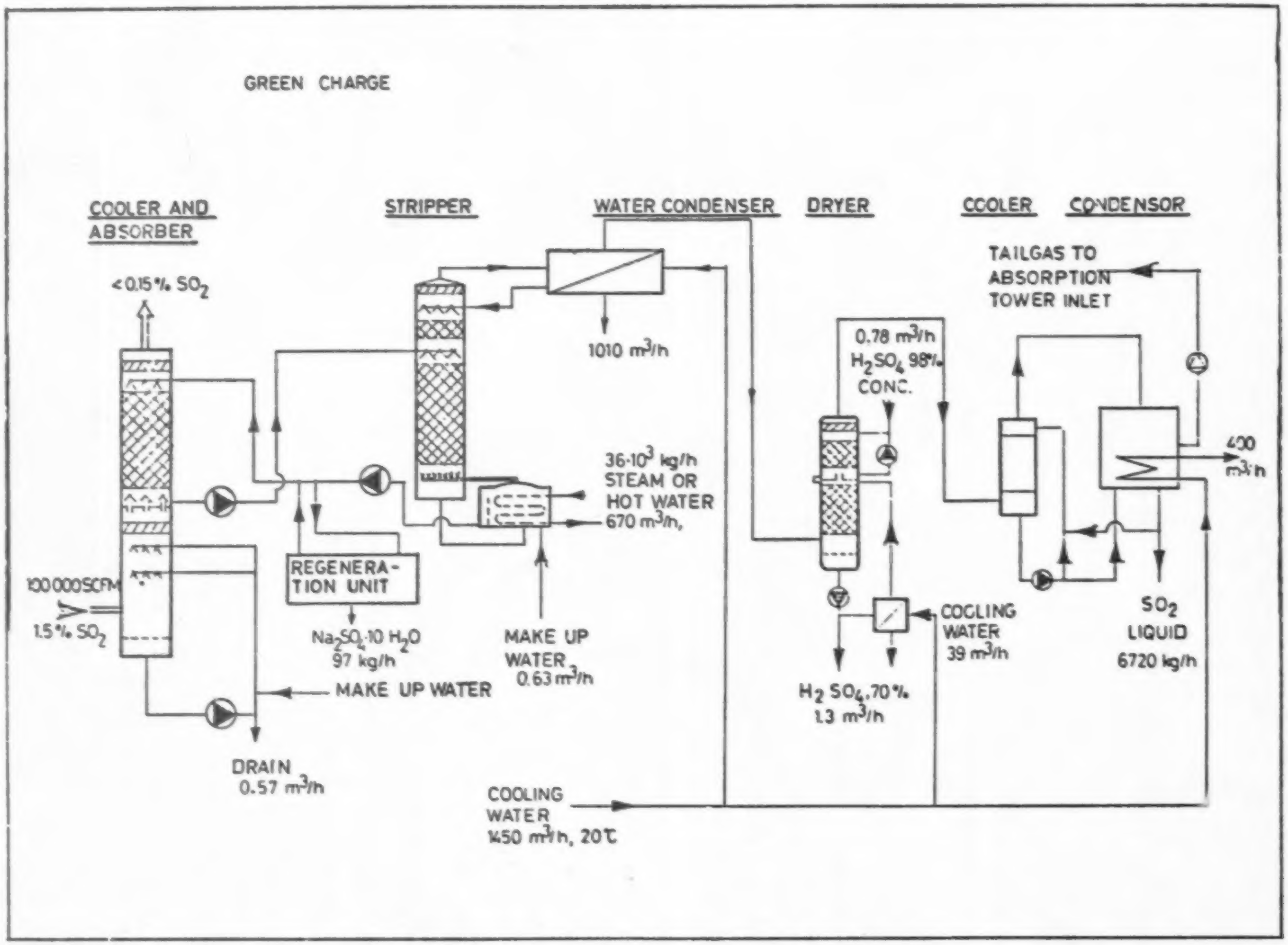

GREEN CHARGE
COOLER AND ABSORBER
STRIPPER
WATER CONDENSER
DRYER
COOLER
CONDENSOR
<0.15% SO_2
100 000 SCFM
1.5% SO_2
REGENERATION UNIT
$Na_2SO_4 \cdot 10\ H_2O$ 97 kg/h
MAKE UP WATER
DRAIN 0.57 m^3/h
1010 m^3/h
$36 \cdot 10^3$ kg/h STEAM OR HOT WATER 670 m^3/h,
MAKE UP WATER 0.63 m^3/h
COOLING WATER 1450 m^3/h, 20°C
0.78 m^3/h H_2SO_4 98% CONC.
H_2SO_4, 70% 1.3 m^3/h
COOLING WATER 39 m^3/h
TAILGAS TO ABSORPTION TOWER INLET
400 m^3/h
SO_2 LIQUID 6720 kg/h

Figure 5-17. Green Charge Reverberatory Furnace Offgas Flakt Citrate SO_2 Control System

Table 5-1. FLAKT-BOLIDEN PROCESS - TECHNICAL DATA SUMMARY

Fläkt-Boliden Process - Technical data (approx.)

		Calcine charge	Green charge
Gas conditions			
Gas volume SCFM		100,000	100,000
Gas temperature °F		400	400
SO_2 concentration % by vol		0.8	1.5
SO_3 "-		0.1%of SO_2 conc.	0.1%of SO_2 conc.
Water content in gas %		6 - 8	10 - 15
Oxygen content in gas %		8	8
Fläkt-Boliden Process			
Required SO_2 removal efficiency	%	90	90
Consumption of low grade steam or	kg/h	31,000	36,000
Hot water (if no steam available)	m^3/h	500	670
Cooling water of 20°C in 40°C out for water condenser	m^3/h	867	1,010
Make-up water	m^3/h	15.4	19.0
Citric Acid (100%)	kg/h	0.5	0.8
NaOH (100%)	kg/h	13	24
Electrical power (incl. fan)	kW	325	325
If an SO_2 liqucfaction system is installed the following additional data will apply			
Production of liquid SO_2	kg/h	3580	6720
Additional consumptions of			
Cooling water	m^3/h	243	439
H_2SO_4 for dryer (98%)	m^3/h	0.51	0.78

After the dryer H_2SO_4 (70%) is returned to a sulfuric acid plant for reconcentration or neutralized.

If NaOH is not available for the sodium citrate solution $NaCO_3$ can be used as well

5.5.4 APPLICATION OF CITRATE PROCESS TO COPPER SMELTER REVERBERATORY FURNACE SO_2 CONTROL

If the citrate system is viewed simply as an extension of the cold water absorption system, its relative simplicity and reliability are evident. As an absorption system it can be viewed as concentrating the sulfur dioxide from the reverberatory furnace to a point where it can then be used as feed to any other subsequent system that may produce either liquid SO_2, sulfuric acid or sulfur. The subsequent systems of course must have been developed satisfactorily.

With steam stripping, the supply of steam at a smelter should not be a critical item since stripping is conducted under vacuum conditions allowing the use of low quality steam or even hot water. However, the system requires additional water to be supplied which could be a problem in some areas.

Operating experience on metallurgical gases, both at full-scale and particularly at the pilot plant scale, indicate the feasibility of the material as an absorbent. The operation of the full-scale plant processing reverberatory furnace gases must still be demonstrated for long periods of time. The record, however, does not indicate that any of the experimental difficulties encountered in all the test work represents fundamental problems that would eliminate this system from consideration.

5.6 COMINCO AMMONIA SCRUBBING SYSTEM

5.6.1 GENERAL

Sulfur dioxide removal from gas streams by ammonia-based scrubbing has been studied intermittently by various groups since the 1880's when a British patent was first issued to Ramsey.[99] Ammonia-based processes are not amenable to throw-away operation because of the cost of ammonia and the solubility and nitrogen value (with chemical oxygen demand) of ammonium salts. Perhaps the best known ammonia scrubbing process is the one developed by the Consolidated Mining and Smelting Company and its operations at Trail, B.C.[100]

The Cominco process can achieve high efficiencies of SO_2 removal over a wide range of SO_2 concentrations well within that encountered by copper reverberatory furnaces. Since the absorbent is a solution rather than a slurry, there are no scaling or plugging problems in the process. The system produces a concentrated SO_2 stream which can be used to produce sulfuric acid, elemental sulfur, or liquid SO_2. The main problem with this process is the loss of ammonia from the system. The ammonia volatility may limit the minimum level of SO_2 emission to 200 to 300 ppm for practical operations and also introduces costs that could produce an economic problem.

The Cominco Smelter is located near the U.S.-Canadian border. The first acid plant to control SO_2 was built for zinc roaster gas in 1916. Since the various systems have been added to adequately control the SO_2, the present SO_2 control at the smelter is 96.6 percent.

Preliminary studies on the recovery of 100 percent SO_2 from roaster gas and reduction of this to elemental sulfur were started in 1932. A number of absorbents were investigated to concentrate the SO_2 from the roaster gas, and ammonia-based scrubbing was finally selected as the most feasible and economical. A 3 ton/day sulfur pilot plant was put into operation in 1934. The experimental work was conducted on lead sintering plant gas.

A semicommercial ammonia base absorption plant operating on zinc roaster gas and a 40 ton/day reduction unit went into production in 1936. A larger absorption plant operating on zinc roaster gas of 5.5 percent SO_2 with tail gas less than 0.2 percent SO_2, a plant to treat the lead sintering machine gas of 0.75 percent SO_2 with tail gas of 0.10 percent SO_2, and two additional reduction units were added, bringing the total rated capacity to 150 ton/day of sulfur.

In 1943, greatly increased supplies of fertilizer were considered essential to the war effort, and a number of changes were made to meet the fertilizer requirements. The SO_2 reduction plants were closed down in 1943, and the 100 percent SO_2 was used to enrich the gas to the contact acid plants and increase their output. Presently, Cominco converts part of the SO_2 into sulfuric acid and part into ammonium sulfate.

5.6.2 PROCESS DESCRIPTION

The schematic of the ammonia scrubbing process for controlling SO_2 from lead sintering plant gas at Trail, B.C. is given in Figure 5-18. Process chemistry is summarized in Appendix T. A total of 300,000 scfm of flue gas from the lead sintering plant containing 0.75 percent SO_2 passes through a humidifying tower and a dust collector before entering the absorption plant. Then, the sulfur dioxide content is absorbed in aqueous ammonia, forming a solution that is essentially ammonium bisulfite.

The gas is treated in two parallel systems, each comprising a lead cooling tower, wood-supported and wood-packed, and three lead absorption towers, also wood-supported and wood-packed. Flow of water in the cooling tower, up to 1,600 gal/min, is countercurrent to the gas flow. The three absorption towers are constructed as a unit having two partitions with the required openings for gas dividing the structure into three towers. The flow of gas is concurrent with the solution in the first tower, countercurrent in the second tower, and concurrent in the third tower.

The circulating solution is pumped from the base of each absorption tower to a distributing spider at the top (flow being 1,200 to 1,500 gal/min in the first two towers and 600 to 800 gal/min in the third). Aqueous ammonia containing about 30 percent nitrogen is added to the circulation. Circulating solution temperature is controlled by passing it through water coolers (aluminum tubes and steel shell) immediately after the addition of ammonia, removing the heat of reaction. Temperature of the circulating solution is controlled at about

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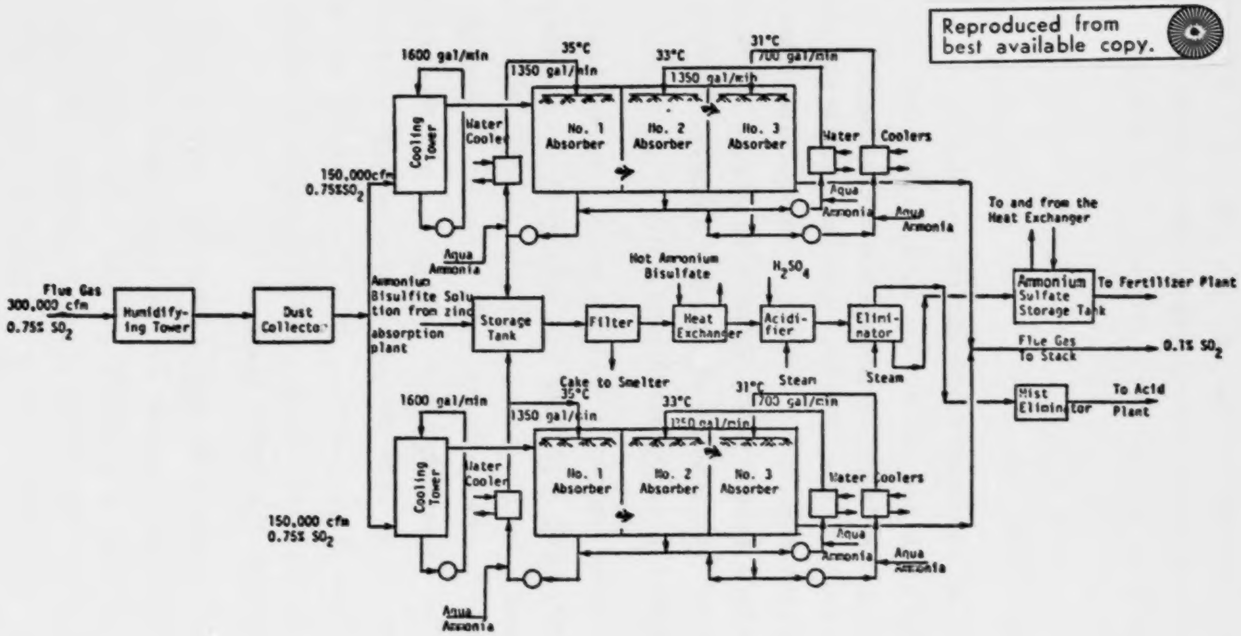

Flue Gas
300,000 cfm
0.75% SO_2
Humidifying Tower
Dust Collector
150,000 cfm
0.75% SO_2
1600 gal/min
Cooling Tower
Water Cooler
Aqua Ammonia
1350 gal/min
35°C
33°C
31°C
1350 gal/min
700 gal/min
No. 1 Absorber
No. 2 Absorber
No. 3 Absorber
Water
Coolers
Aqua Ammonia
Ammonium Bisulfite Solution from zinc absorption plant
Storage Tank
Filter
Cake to Smelter
Hot Ammonium Bisulfate
Heat Exchanger
H_2SO_4
Acidifier
Steam
Eliminator
Steam
To and from the Heat Exchanger
Ammonium Sulfate Storage Tank
To Fertilizer Plant
Flue Gas To Stack
0.1% SO_2
Mist Eliminator
To Acid Plant
150,000 cfm
0.75% SO_2

Figure 5-18. Flow Diagram Cominco Ammonia Scrubbing Process

35°C in the first tower and about 2°C lower in each of the succeeding towers. Water from the tube coolers is used in the cooling towers before wasting to the sewer.

Solution is bled forward from one tower base to the next. The circulating solution is bled off the first tower to storage provided by two 60,000 gal lead lined wood stave tanks. The bled absorption solution from the zinc roaster ammonia absorption plant is also stored in these two tanks.

Mixed ammonium bisulfite solutions from the lead sintering and zinc roaster absorption plants, stored in the two bisulfite storage tanks, are filtered through Shriver presses using vinyon cloth and filter aid, and the filtrate is stored in a 200,000-gallon lead lined wood stave tank. The filter cake is returned to the smelter. The filtrate goes to a heat exchanger which is heated by hot ammonium sulfate solution. It is then further heated with steam in a stainless steel tubular heater, and mixed with sulfuric acid in a Pachuca-type acidifier. Two acidifiers are installed, one operating, one standby. The evolved sulfur dioxide gas and solution overflow into the eliminator, where the remainder of the gas is boiled out of the ammonium sulfate solution with direct steam. Two eliminators are installed, one operating in series with each acidifier. These are constructed of steel, lined with Pyroflex and acidproof bricks, and packed with spiral rings.

From the eliminator, the ammonium sulfate solution, substantially free of sulfur dioxide, flows by gravity to a 200,000-gal ammonium sulfate storage tank. This tank is all wood stave contruction and lead lined. Coils are installed in the pump tanks, to preheat the bisulfite feed to the acidifier and in the heat exchanger. Aqueous ammonia is added to the ammonium sulfate in the pump tank to neutralize the free acid and produce a slightly ammoniacal solution to minimize corrosion of equipment. The ammonium sulfate solution from the storage tank (containing about 42 percent ammonium sulfate) is pumped to the fertilizer plant.

The gas from the eliminator containing sulfur dioxide and water vapor presently go to an acid plant after passing through a mist eliminator. These gases could also go to an SO_2 reduction system using coal to produce elemental sulfur.

5.6.3 THE APPLICATION OF THE COMINCO AMMONIA PROCESS TO CONTROL COPPER REVERBERATORY FURNACE OFFGAS

The most significant operating parameters in the absorption step have been shown to be:

1. Solution temperature
2. Total concentration of SO_2 and NH_3 in solution
3. Concentration of individual ammonium salts (sulfite, bisulfite, and sulfate) which also determines pH
4. Ratio of liquid to gas flow
5. Type of internal column construction

Griffin[101] showed that the equilbrium absorption of SO_2 is enhanced by

1. Decreasing the solution temperature
2. Minimizing the total SO_2 concentration in the solution

Ammonia losses are reduced by

1. Decreasing the solution temperature
2. Minimizing the total NH_3 concentration in solution

At Cominco, plant control is based on analysis of the inlet and tail gas and circulating solution from each absorption tower. Solutions are analyzed for pH. Aqueous ammonia is added to the solution to control the pH. At low pH, there is no SO_2 absorption and very high pH results in very high NH_3 losses. So the solution pH has to be maintained within a narrow range to give good SO_2 absorption and reasonably low NH_3 losses. This is achieved at Cominco by adding aqueous ammonia to each absorption tower and controlling the solution temperature to each absorption tower.

A serious problem that has been encountered with most of the ammonia scrubbing systems is the formation of an opaque fume in the exit gas stream. The fume is partly attributed to gas-phase reactions of ammonia, SO_2, and water forming ammonium sulfite, which, due to its small size, is not efficiently removed by a conventional mist eliminator.[102] Wet electrostatic precipitators have been used at some installations to eliminate this problem. Cominco reported adequate control of the fume when operating with low liquid temperature to reduce the ammonia and SO_2 losses, and pretreating the gas before the absorbers. Pretreatment of the gas to decrease the particulate loading reduces the condensation nuclei on which ammonium sulfate could form. Cominco has conducted pilot tests and is currently preparing to install (by 1981) new equipment in their ammonia SO_2 control system to minmize or eliminate the stack opacity problem. The approach includes establishing critical pH and temperature ranges within the primary scrubber. Basic work on this technique has been done by Catalytic, Inc. (Philadelphia, Pa), which hold patents with emphasis on application to utilities.

If natural gas is the source of the synthesis gas used to produce ammonia, then the same energy-related question arises with this process as is present with the reduction to sulfur processes. (Refer to Section 5.8). The ammonia synthesis gas should be produced from coal (not now generally done in the U.S.) for compatibility with current energy planning and future cost effectiveness.

5.7 WELLMAN-LORD PROCESS

5.7.1 GENERAL

The Wellman-Lord SO_2 recovery process was developed by Davy Powergas in the late 1960s. Thirty commercial installations throughout the world are presently either in operation or in design or construction. Half of these are in Japan. The Wellman-Lord process has been successfully applied to SO_2 absorption from sulfuric acid plants, Claus unit tail gases, as well as oil and coal-fired boilers. However, it has never been applied to the metallurgical industry. All the installations currently operating in the U.S. have an $SO2$ removal efficiency of greater than 90 percent, and an on-stream time of greater than 97 percent for the absorption step. The Japanese installations have an SO_2 removal efficiency of greater than 95 percent with an on-stream time of greater than 98 percent.

The process provides a method by which the SO_2 from a weak stream can be absorbed by chemical reaction with an alkaline scrubbing liquor. The SO_2 is later desorbed by a heating process in which the SO_2 appears in a concentrated form and the absorbing solution is regenerated for recycling to the scrubber. The strong SO_2 gas resulting from the above absorption and desorption can be further processed to sulfuric acid, elemental sulfur, or liquid SO_2.

Even though this process has considerable full-scale experience at power plants and refineries, its use for processing reverberatory furnace offgas has not been demonstrated and would require additional confirmatory testing.

5.7.2 PROCESS DESCRIPTION

Figure 5-19 gives the schematic of the Wellman-Lord process. Chemistry in the process is discussed in Appendix U. The flue gas is first led to a gas pretreatment unit where it is cooled down, and the particulate matter is removed. It then enters the SO_2 absorber, which is a simple gas-liquid contacting device with two or more absorption stages. The absorber can be designed to reduce SO_2 concentration to the required level and can accommodate a wide range of turndown conditions. The absorption step is free of scaling problems.

Apart from the conversion of sodium sulfite to sodium bisulfite, the adsorber also produces some nonregenerable and therefore undesirable oxidation products. Contact of the scrubbing solution with oxygen in the flue gas will yield Na_2SO_4 according to

$$Na_2SO_3 + 1/2\ O_2 \longrightarrow Na_2SO_4$$

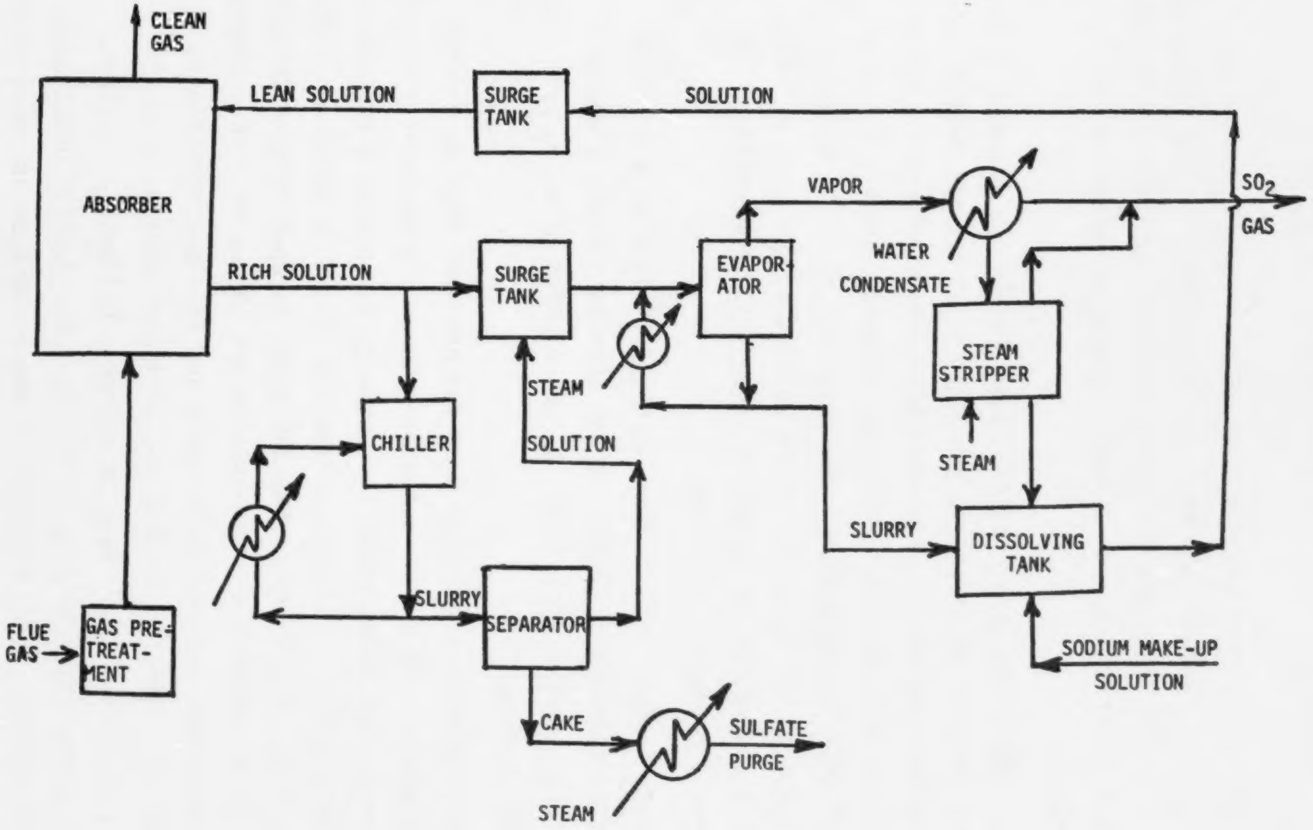

CLEAN GAS
ABSORBER
LEAN SOLUTION
SURGE TANK
SOLUTION
RICH SOLUTION
SURGE TANK
VAPOR
EVAPORATOR
WATER CONDENSATE
SO_2 GAS
STEAM STRIPPER
STEAM
CHILLER
STEAM
SOLUTION
STEAM
SLURRY
DISSOLVING TANK
SLURRY
SEPARATOR
FLUE GAS
GAS PRETREATMENT
SODIUM MAKE-UP SOLUTION
CAKE
SULFATE PURGE
STEAM

Figure 5-19. Flow Diagram for Wellman-Lord Process

The presence of SO_3 in flue gases would also produce Na_2SO_4

$$2\ Na_2SO_3 + SO_3 + H_2O \longrightarrow Na_2SO_4 + 2\ NaHSO_3$$

Since Na_2SO_4 represents a loss of Na^+ ion, it has to be purged from the system. The Na^+ ion is replaced by the injection of NaOH or Na_2CO_3 into the scrubbing circuit. In order to minimize the makeup requirements, the oxidation needs to be suppressed in the absorber.

The liquid/gas (L/G) ratio is kept low in the absorber. The high concentration of salts and low water load has the effects of lowering oxygen absorption, reducing heat demand on the evaporator/ crystallizer, and reducing the size of vessels, pumps and piping. Because of this low throughput, the absorbent fluid is recirculated at each stage of the tower to assure wetting of the tray or packing. Since absorption of oxygen is liquid-film controlling, the low L/G ratio minimizes oxidation.

$NaHSO_3$ is more soluble than Na_2SO_3. By feeding a strongly concentrated solution of Na_2SO_3 to the absorber, scaling and salt precipitation are not experienced since reaction with SO_2 produces the soluble $NaHSO_3$.

Sodium bisulfite solution from the absorber goes to a surge tank from where it is fed at a steady rate into a forced-circulation evaporator-crystallizer, which is heated by low pressure exhaust steam. Here the SO_2 is released from the bisulfite which is regenerated to the sulfite. A mixture of SO_2 and steam escapes through the top. This gas is cooled to 120°F to condense out the water. The condensed water is saturated with sulfur dioxide and is steam stripped to remove the SO_2. The SO_2 leaving the stripper combines with SO_2 from the evaporator and is lead to either a sulfuric acid plant, elemental sulfur plant, or liquid SO_2 plant for further processing. The sodium sulfite slurry produced in the evaporator is redissolved in a dissolving tank with recycled condensate from the condenser system. The resulting lean solution flows to another surge tank and is recycled to the absorber.

Fluctuations in the absorber and regeneration sections are stabilized by routing the solutions from each section through surge tanks. In addition, the regeneration section can be remotely located from the absorber section. The regeneration section can shutdown completely for scheduled maintenance without interrupting SO_2 removal in the absorber section.

To control the level of inactive sodium sulfate in the solution, a small sidestream is sent to a purge treatment section to remove the sulfate and return active solution to the chemical section. The sodium sulfate is precipitated from the solution by cooling in a chiller-crystallizer. With controlled crystallization, the sulfate precipitates in a much greater proportion than the other sodium compounds. Thus, the solid phase is enriched in sulfate while the liquid phase becomes leaner. The solid phase is separated from the liquid, and the latter is returned to the absorber. The solid phase can be dried for sale or for disposal.

5.7.3 APPLICATION OF THE WELLMAN-LORD SYSTEM FOR REVERBERATORY FURNACE SO_2 CONTROL

Sulfur dioxide absorption efficiency is controllable by adjusting process parameters at the absorber with most operating systems producing 90 to 92 percent SO_2 recovery.

The SO_2 inlet concentration has a marked effect on the utility requirements. For a given amount of SO_2 to be recovered, as the inlet concentration in the flue gas decreases, the required amount of heating steam and cooling water increases. As the concentration of oxygen increases, the size of the purge treatment section and the chemical makeup requirement will increase.

Oxidation of a small amount of the solution (sodium sulfite to sodium sulfate) in the Wellman-Lord absorber creates the need to purge a portion of the solution from the system. This purge has two effects: (1) a chemical makeup requirement, and (2) a potential waste disposal problem. About 1-1/2 to 3 percent of the SO_2 in the flue gas entering the absorber will take part in the oxidation reaction forming the non-reactive sodium sulfate for boiler control applications as claimed by Davy Powergas.[103] Other estimates are 10 percent.[104] Many weak smelter gases have much higher oxygen content than power plant flue gases, due to stream dilution by infiltrating air at ESP's, waste heat boilers, and leaky hoods and flues. These higher oxygen concentrations will presumably result in high sodium sulfate formation. Also, there is high SO_3 concentration in smelter gases which will further increase sulfate formation. Fractional crystallization has been used to minimize the purge stream and the chemical makeup requirements.

The concentrated purge stream from this system can be dried for sale or for disposal. Potential markets exist for this material in some areas of the U.S.

With the absorption advantages of high concentration solution scrubbing, L/G ratios are significantly less than those required for the lime/limestone process, and power requirements for absorbent recirculation are correspondingly less. However, power requirements in the forced-circulation evaporator/crystallizer section of the regeneration area tend to compensate for this saving.

Steam requirements in the evaporator/crystallizer constitute a significant proportion of the total energy needs of the process. Single pass evaporation steam demands appear to be as high as 12 lb per lb SO_2, but use of a double pass unit will reduce steam consumption by about 40 percent.[105]

Although applicability to weak smelter gases has not been commercially demonstrated, the following advantages of the process are noted:

1. Sulfur dioxide absorption capability is excellent and as a clear solution scrubbing system, equipment maintenance, and operation poses no special problems.

2. The process generates a high purity stream of SO_2 - around 85 percent, or higher if appropriate drying facilities are added. This provides options between sulfuric acid, elemental sulfur, or liquid SO_2.

3. The process has enjoyed considerable commercial application and it appears that plants can be designed with a high degree of confidence as indicated by the performance guarantees being provided with the Wellman-Lord installation for the Northern Indiana Public Service Company (NIPSCO) on a 115 Mw coal-fired utility boiler.

4. The process can handle wide swings in SO_2 concentration.

The principle disadvantages of this system appear to be:

1. Oxidation in the absorbent, resulting in purging and loss of high cost sodium ions. Fractional crystallization of the purge stream to separate and regenerate sodium sulfate is possible, but this approach is associated with both additional capital and operating costs.

2. Total energy requirements of the overall process, i.e., gas conditioning or SO_2 absorption and regeneration are appreciable and constitute a major part of the total overall operating costs.

As mentioned previously, testing with actual reverberatory furnace offgas is required to confirm transfer of this technology to the smelting industry.

5.8 COAL REDUCTION

5.8.1 GENERAL

Various reduction systems that have been used for reducing SO_2 to elemental sulfur at smelters were reviewed. The Claus process and Bureau of Mines Citrate process both utilize natural gas for SO_2 reduction when H_2S is not available. The ASARCO brimstone process uses natural gas directly as the reducing agent. Due to the present and future supply situation for natural gas, it does not appear practical to consider it as a reducing agent for SO_2. Coal, which is in abundant supply in the U.S. and probably will be used much more frequently for reverberatory furnace firing in the near future, seems to be the most logical reducing agent if sulfur is required as the end product of an SO_2 control system.

Sulfur dioxide reduction with carbon has been practiced in the past by a few smelters. The Boliden process operated at the Ronnskar Smelter in Sweden was employed for gases relatively rich in SO_2. At this plant, part of the smelter gas containing 11 percent SO_2 is diluted with air, preheated, and then blown through a special gas producer filled with coke. The following reactions occur:

$$C + O_2 \rightleftharpoons CO_2$$

$$CO_2 + C \rightleftharpoons 2\,CO$$

$$SO_2 + C \rightleftharpoons CO_2 + 1/2\ S_2\ (g)$$

$$SO_2 + 2C \rightleftharpoons 2CO + 1/2\ S_2\ (g)$$

A number of minor reactions also occur

$$CO + 1/2\ S_2\ (g) \rightleftharpoons COS\ (g)$$

$$C + S_2\ (g) \rightleftharpoons CS_2\ (g)$$

$$H_2O + C \rightleftharpoons CO + H_2$$

$$H_2 + 1/2\ S_2\ (g) \rightleftharpoons H_2S$$

The reducing gas thus prepared is added to the remainder of the smelter gas and both are passed through a catalyst chamber at 400° to 600°C. The catalyst consists of coarse pieces of ferric oxide and alumina. The following reactions take place:

$$SO_2 + 2\,CO \rightleftharpoons 2\,CO_2 + 1/2\ S_2\ (g)$$

$$SO_2 + 2\,H_2 \rightleftharpoons 2\,H_2O + 1/2\ S_2\ (g)$$

$$SO_2 + 2\,COS \rightleftharpoons 2\,CO_2 + 3/2\ S_2\ (g)$$

$$SO_2 + 2\,H_2S \rightleftharpoons 2\,H_2O + 3/2\ S_2\ (g)$$

$$SO_2 + CS_2 \rightleftharpoons CO_2 + 3/2\ S_2\ (g)$$

These reactions do not go to completion so that the exit gas always contains some sulfur compounds. The gas is finally passed through a cooler where the sulfur is condensed; sulfur mist from the cooler is similarly removed by passing the gas through a Cottrell precipitator.

Cominco, at their Trail, B.C. Smelter, used a similar method for SO_2 reduction. The SO_2 gas concentration was essentially 100 percent and was obtained from their ammonia system (Section 5.6.3).

In the Orkla process used at Rio Tinto Co., Ltd., the smelting and SO_2 reduction feed to the furnace consists of the ore, fluxes, and a certain amount of coke. In the lower parts of the furnace the sulfur is oxidized to SO_2. In the top part of the furnace a reducing atmosphere is created due to the presence of coke, and when the gases from the bottom containing SO_2 pass through this section of the furnace, SO_2 is reduced to sulfur. The gases are then passed through a hot Cottrell precipitator and thence into a condenser where the bulk of the elemental sulfur is liquified; a further small amount of sulfur is recovered when the gases are passed through a second (cold) Cottrell precipitator. A maximum of approximately 55 percent of the input SO_2 was converted to sulfur. Details of the Orkla system are presented in Appendix V as a reproduction of a paper presented by Rio Tinto Co., Ltd., personnel. It contains a discussion of the SO_2 reduction chemistry that is applicable to the reverberatory furnace.

The Resox process, developed by Foster Wheeler Corporation, reduces sulfur dioxide to sulfur by using crushed coal. This system is described in detail in Appendix W. It is claimed that it can handle a wide range of inlet gas compositions and does not require gas cleaning, drying or dust removal systems. Sulfur dioxide rich gases (20 to 30 percent concentration) are reacted with crushed coal at temperatures as low as 1,200°F in a reactor vessel. The SO_2 stream is reduced to gaseous elemental sulfur and the liberated oxygen combines with a portion of the coal carbon to form carbon dioxide. The gases leave the reactor and enter a sulfur condenser where the sulfur is condensed to molten elemental sulfur. This system was the tail end unit for the Scholz steam plant system using the activated coke adsorption system developed in Germany to concentrate the sulfur dioxide.

Based on experience at smelters with coal reduction processes, it appears that relatively high concentrations of input SO_2 gas has been used. There has not, however, been any major effort to use these processes on reverberatory furnace offgases. Furthermore, the well known water gas reaction with coal and steam generating CO and H_2 could be involved using coal reduction which then allows consideration of this process as a gaseous reduction. Separate production of the reducing gas from coal would allow better system control but introduces additional complexity, and cost which may not allow use of this technique. Costs must be compared to production and shipping sulfuric acid.

5.8.2 COMINCO COAL REDUCTION SYSTEM

The SO_2 gas from the Cominco ammonia concentration system at nearly 100 percent SO_2 (Section 5.6) was originally reduced by coal to produce sulfur. Cominco at Trail B.C. operated the coal reduction plant from 1936 to 1943 with a rated capacity of 150 ton/day of sulfur.[106]

The reduction plant as mentioned in Section 5.6 was shutdown in 1943 when the demand for sulfuric acid for fertilizer production exceeded the output of the acid plants. The reduction process employed the well-known reaction between sulfur dioxide and incandescent coke. The reaction is slightly exothermic, but cannot support itself, so some oxygen must be added to the process furnace to makeup the heat lost.

The reducing reaction does not go to completion in the furnace. Various side reactions take place, so the exit gases contain considerable quantities of carbonyl sulfide and CO, and at times, small amounts of carbon bisulfide as well as elemental sulfur and CO_2. Some SO_2 is added to the exit gases for catalytic conversion of this carbonyl sulfide to sulfur by reaction with SO_2.

Gases from the top of the furnace, mixed with the required amount of SO_2 to convert the carbonyl sulfide, pass through a cyclone where coke dust is removed and then pass through a precatalyst column which is a steel vessel, lined and packed with fire-brick, where a greater part of the carbonyl sulfide is converted. The gas then passes through a waste heat boiler for cooling to the optimum temperature for completion of the catalysis and then through the catalyst column, a vessel similar to the precatalyst column but packed with catalyst. From the catalyst column, the gas passes through a second waste heat boiler where it is cooled so that all the sulfur is condensed as a liquid or a mist. The sulfur mist is removed from the tail gas in a electrostatic precipitator, and the tail gas is scrubbed with water.

Liquid sulfur from the waste heat boiler and the electrostatic precipitator runs into a settling pot and is pumped through a steam-jacketed Shriver press for removal of a very small quantity of extremely fine carbon which gives a greenish tinge to the sulfur. From the filters, sulfur at a purity exceeding 99.99 percent runs into heated tanks and is pumped to storage blocks.

With coal availability and a concentrated SO_2 stream, the extensive 7 year experience with this system would indicate that reduction to sulfur has been demonstrated as feasible technology. The requirement for concentrated SO_2 could, of course, reduce the economic desirability of this approach. The storage flexibility of sulfur compared to sulfuric acid could strongly influence the choice of this system in any given situation. It should also be noted that the minimum concentration of SO_2 that can be efficiently processed with this system has not been determined.

5.9 COMPARISON OF PRIMARY COPPER REVERBERATORY FURNACE AND POWER PLANT EMISSION CHARACTERISTICS

5.9.1 INTRODUCTION AND SUMMARY

Since most FGD systems have been developed for utility boiler offgases, an investigation into the differences between these gases and reverberatory furnace offgases was conducted to determine if the technology could be transferred.

It became clear on review of available reverberatory furnace data that it was limited in consistency and quantity. The comparison indicates that furnace gases have an O_2 content slightly higher, CO_2 content about the same, H_2O considerably higher for green charge furnaces and about the same for calcine charge, and particulate considerably higher than the power plant gases. Particulate can, of course, contain all of the trace metals found in ores being processed. The effects of these metals, which can either cause physical plugging or effect chemical or catalytic reactions, have not specifically been determined. However, the experience in Japan indicates that the lime/limestone nonregenerative and MgO regenerative systems can be used on either utility boilers or reverberatory furnaces. The effects of trace metals that may pass through gas precleaning systems on the citrate and ammonium regenerative systems also do not seem to be significant since the systems have been demonstrated on metallurgical gases. Whether the Wellman-Lord system could be used has yet to be demonstrated. Experience also indicates that the coal reduction systems can be used with smelter gases.

Table 5-2 shows a comparison of conditions applied to the Mitsubishi lime/limestone systems for oil-fired boilers, sintering plants, and the reverberatory furnaces at the Onahama Smelter.

5.9.2 GAS COMPARISON

Reverberatory furnaces usually operate with a draft of about minus 0.1 inch water gage, and the combustion is usually regulated

ITEM	EMMISION SOURCE	Oil-Fired Boilers	Sintering Plants (Steel Mills)	Copper Smelter
Inlet SO_2	ppm (Volume)	500 - 1,500	600 - 1,200	20,000 - 29,000
SO_2 Removal	%	90 - 99	90 - 97	90 +
Absorbent Utilization in Scrubber	%	90 - 99	95 - 99	- 99
Scrubber Control pH	-	6.5 - 7.0 (Lime) 4.0 - 5.8 (Limestone)	6.5 - 7.5	3 - 3.5 ① 9 - 10.5 ②
Oxidation in Scrubber	%	30 - 100	70 - 100	0 - 20
Slurry Concentration	% (Weight)	10 - 14	10 - 14	10 - 13
Inlet Gas Composition		(Pre-cooler Inlet)	(Pre-cooler Inlet)	(Scrubber Inlet)
O_2	% (Volume)	3 - 6	12 - 17	6
CO_2	% (Volume)	9 - 12	4 - 8	10
H_2O	% (Volume)	9 - 12	6 - 12	23
Dust	Grains/scf	0.0085 - 0.0175 (ESP Outlet) 0.04 - 0.08 (Boiler A/H Outlet)	0.0175 - 0.04 (ESP Outlet)	0.06
Remarks		One Scrubber System 12 Units Two Scrubber System 1 Unit	Inlet Cl : 20 - 50 ppm (as HCl) Inlet Oily Matter: - 0.025 gr/scf Dust Components: Fe, Mn, Si, Pb, K, Na, Ca, Mg, Al, Zn, Cu, etc.	Two Scrubber System ① No. 1 Scrubber ② No. 2 Scrubber

Table 5-2. OPERATING DATA OF MHI FGD SYSTEMS

so that a slight excess of air is used. The analyses of reverberatory flue gases generally will be within the following ranges.[107]

N_2 - 72 to 76 %
CO_2 - 10 to 17 %
CO - 0.0 to 0.1 %
O_2 - 5 to 10 %
H_2O - 4.0 to 10.0 %
SO_2 - 1.0 to 2.0 %

The amounts of CO_2 and H_2O will depend upon the fuel used and the amount of moisture in the charge; the SO_2 content will depend upon the sulfur elimination from the charge. A large part of the free oxygen found in the flue gases may be due to leakage of air through charging holes and other openings in the furnace. The gases will leave the furnace at a temperature of 1,800° to 2,300°F (980° to 1,260°C).

Power plant boilers will generally be within the following ranges.[108]

N_2 - 80 to 85 %
CO_2 - 10 to 14 %
O_2 - 3 to 8 %
SO_2 - 0.05 to 0.15 %
H_2O - 4 to 10 %

Gas analyses obtained from representative smelters using green charge (no roasters) with oil, gas, or coal and boilers using oil and coal are shown in Table 5-3. These values tend to be in the range noted in the above summary with variations resulting from individual measurements and operating conditions.

5.9.3 DUST COMPARISON

The amount of dust emitted by reverberatory furnaces will depend upon the fineness of the particles in the charge, the method of charging, etc. The dust itself may include anything in the furnace charge or formed by decomposition during melting which is fine enough to be carried by the gas current.

	Kennecott Hurley Natural Gas Green Charge (1) (2)	Kennecott Hayden No. 2 Oil (3)	Magma San Manuel Natural Gas or Oil Green Charge (4)	Onahama Smelter Japan Oil Green Charge (5)	Phelps Dodge AJO Natural Gas (6)	Boiler Oil (7)	Power Plant Coal-Fired (8)	Power Plant Natural Gas Dry Basis (9)
CO_2	8.3, 2.0	7.1	8.3	10		11-15	10-14	9.38
SO_2	3.0 (High) 0.74 - 0.87, 1.07	0.6	0.7 - 1.0	2.0 - 2.9 (OX Enrich)		0..082 -0.14 0.088	0.11 - 0.17	
H_2O	19.1 (High) 4.0-7.0, 5.5	7.6	19.24	23		8 - 10	4-7	
N_2	67.6		69.71			81-85	80-82	87.33 +Ar by Diff.
O_2	2.0,17.2	8.9	10-15	6		3-6	5-8	2.54
SO_3	0.02,0.022	0.0026				0.0009-0.002	0.0009-0.008	
NO_x	0.0007					0.026-0.04	0.031-0.12	0.05
CO							0.0015-0.006	0.513
HC								.19
Volume Flow Rate SCFM	200,000		350,000	110,000				
Dust GR/SCF	0.45-0.97			0.6 (Before ESP) 0.06 (After ESP)	0.9			

(1) Data taken at different times shown by different values - 1-2% OX enrichment
(2) Reference 39
(3) Reference 40
(4) Reference 41
(5) Reference 42
(6) Reference 43
(7) References 44, 45
(8) References 45
(9) References 46

Table 5-3. GAS CHARACTERISTICS COMPARISON

Fume, as differentiated from dust, refers to material which has been volatilized or sublimed, and then condenses when the gases become cooler. The most important constituents found as fine particulate in copper smelters are:

1. The lower, volatile oxides of arsenic and antimony As_2O_3 and Sb_2O_3.
2. Oxides of other volatile metals--e.g., PbO and ZnO.
3. Condensed water vapor.
4. Sulfuric acid and sulfates. A certain amount of SO_3 gas is formed from the further oxidation of SO_2, and the higher the SO_2 content the greater will be the amount of SO_3. The SO_3 combines with water vapor to form droplets of sulfuric acid (H_2SO_4 + water), or it may combine with certain basic oxides, notably ZnO, to form $ZnSO_4$.

In practice, the dust and condensed fume are often mixed and collected as a single product; usually the collected product is called a dust--e.g., flue dust or Cottrell dust.

Table 5-4 is a comparison of constituents in the particulate for reverberatory furnaces and power plants. Table 5-5 shows the total grain loading comparison.

The power plant dust contains less minerals, as would be expected.

Additional reverberatory furnace dust analysis (Table 5-5) shows iron will definitely be present. It is also of interest to note sulfur present probably as metal sulfide.

5.10 APPLICATION OF FGD SYSTEMS TO REVERBERATORY FURNACE OFFGASES

5.10.1 CONTROL OF GAS VOLUME FLOW RATE AND SO_2 CONCENTRATION

As discussed in Section 3.0, the volume flow rate of gases leaving the reverberatory furnace can be reduced by several techniques including sealing of the furnace and oxygen enrichment. The gas volume flow rate in current U.S. practice is strongly influenced by leaks with resulting large quantities of dilution air. For

Table 5-4. PARTICULATE OUT OF REVERBERATORY FURNACE AND POWER PLANT

Element	Kennecott (1) Hurley % b.w.	Power (2) Plant % b.w.	Power (3) Plant % b.w.	
Cu	1-25	0.02-0.065	N.D.	Inlet to ESP
Fe	2-20	0.9-11	7.9	
Mo	0.1 - 0.5	0.004-0.03		
Pb	0.2 - 2.0	0.01-0.21	0.005	
Si	19-60			
Al	2.0			
As	0.01 - 0.15	0.004-0.008		
Ba	0.5	0.02-0.2		
Hg	None			
Mg	0.2			
Mn	0.01	0.01-0.04	0.016	
Ni	.001 - .02	0.02-0.06	0.010	
Sn	0.1 - 1.0	0.002-0.007		
W	None			
Zn	2.0 - 30	0.02-0.21	0.0043	
Cd		0.001-0.008	0.0002	
Sb		0.02	0.018	
Se			0.005	
Cr		0.004-0.06	0.0079	
V		0.04-0.12	0.026	
B				
Te				
Ca	0.4			
Al	2.1			
Be				
Ti				
Co				

NOTE - Elements may be in the form of oxides or sulfides

(1) Reference 39

(2) Reference 45

(3) Reference 47

Table 5-5. ANALYSES OF SOME DUSTS (in percent)

Constituent[c]	Cu	As	Sb	ZN	Pb	Bi	S	SiO_2	Fe	Ca	Al_2O_3
Anaconda: Reverberatory furnace; collected under waste-heat boilers. Sample No. 1[a]	22.0	11.6	12.0	9.2	3.4	1.4	0.7	9.0	14.2	0.4	1.5
Anaconda: Reverberatory furnace dust;collected under waste-heat boilers. Sample No. 2[a]	19.7	22.0	0.3	3.5	2.3	1.5	0.1	5.7	10.7	0.6	2.7
Roan Antelope: Reverberatory furnace dust[b].	31.22	-	-	-	-	-	5.7	19.82	3.9	2.2	11.37

[a] Barnard, E.A., and Tryon, George, Waste-Heat Boiler Practice at the Anacomda Reverberatory Plant: Am. Inst. Min. & Met. Eng. Trans., Vol. 106, p.230, 1933.

[b] Wraith, C.R., Smelting Operations at Roan Antelope, Idem., p.214.

[c] As oxides or sulfides

example, the volume flow rate from one Onahama reverberatory furnace system is 55,000 scfm compared to a range of 60,000 to 120,000 scfm at typical U.S. Smelters. Sulfur dioxide concentration (Section 2.0) varies from 0.5 percent to 1.5 percent for U.S. reverberatory furnace systems as compared to 1.5 percent to 2.6 percent for Japanese reverberatory furnace systems partly because of improved sealing.

Thus, in considering the application of FGD systems, the reduction of the gas volume flow rate and the increase of the SO_2 concentration must be the first step to minimize the size and increase the efficiency of these systems. As discussed below, there will be some systems that would not be applicable if gas volume flow rates and SO_2 concentration are maintained as is present practice with reverberatory furnace operation. In all cases, reduction of volume flow rate will reduce system size with obvious capital and operating cost savings.

5.10.2 BLENDING - SULFURIC ACID PLANT

Blending of gases from the main emitting equipment to produce a gas stream of sufficiently high concentration (to be processed directly in a sulfuric acid plant) is potentially possible if a fluid bed roaster is used. Consider the following typical example:

Reverberatory volume flow rate - 100,000 scfm at 0.5% SO_2
Converter volume flow rate (2 operating) - 100,000 scfm at 4.0% SO_2
Fluid bed roaster volume flow rate - 50,000 scfm at 11.0% SO_2

If all of these gases are blended, a combined SO_2 concentration of 4.0 percent is obtained. As an average flow this would probably be sufficient to operate a single contact sulfuric acid plant autothermally most of the time. It is probably too low to practically operate a double contact plant autothermally. The single contact acid plant will effectively collect an average of at least 96 percent of the input SO_2.

If the reverberatory furnace gases are reduced to that presently being produced at the Onahama Smelter, then the following conditions would be present:

Reverberatory furnace volume flow rate - 55,000 scfm at 0.5% SO_2

Converter volume flow rate (2 operating) - 100,000 scfm at 4.0% SO_2

Fluid bed roaster volume flow rate - 50,000 scfm at 11.0% SO_2

With the above conditions, the blended SO_2 concentration would be approximately 4.8 percent. This is probably marginal for operation of a double contact plant, but is sufficient for operation of a single contact plant to maintain autothermal conditions. In any case, the lower the offgas volume and the higher the SO_2 concentration, the more applicable becomes the blending technique. Since relatively little additional equipment (except for acid plant capacity) is required, it would appear that this approach has economic advantages.

5.10.3 LIME/LIMESTONE GYPSUM SYSTEMS

As discussed in Section 4.2, the lime/limestone gypsum system is currently in operation on reverberatory furnaces at the Onahama Smelter in Japan. The SO_2 concentration to this sytem is currently 2.5 to 2.8 percent. Lower SO_2 concentrations will actually allow this system to become more efficient in terms of sulfur capture. However, if this lower concentration is obtained by dilution, then gas handling equipment will be inefficiently enlarged. If the reduced concentration is obtained by reducing sulfur elimination in the furnace, then this advantage can be efficiently exploited.

Because of the large quantities of water (sea water) available adjacent to the smelter, very little effort is given to reducing the water requirements. It is expected, as discussed in Section 4.2, that the water required can be reduced to the range of 5,400 gal/hr.

The work at Duval also indicates that at least at the lower (0.5 percent) SO_2 concentrations, the efficiency of a lime milk absorbent system operating with a TCA absorber design can be 99 percent with 96-98 percent availability.

It can be expected that the lime/limestone system can operate satisfactorily with the current reverberatory furnace SO_2 concentration of 0.5 to 1.5 percent. In the lower portion of this range where fluid-bed roasters are used, the reduced quantity of SO_2 that needs to be processed will produce a lower quantity of solid waste product and therefore will minimize handling and disposal. Thus, the application of a lime/limestone system to those smelters using fluid-bed roasters would be most applicable. This would be particularly the case where the smelter may be having difficulty in selling the sulfuric acid that is being made from the roaster and converter gases. Space for disposal of the solid waste product is readily available for most smelters.

5.10.4 MAGNESIUM OXIDE SYSTEM

As discussed in Section 5.4 the magnesium oxide system has been operated satisfactorily on reverberatory furnace offgas at the Onahama smelter in Japan. This system produces a concentrated gas stream from 10 to 13 percent SO_2 which can be used directly in a double contact (or single contact) sulfuric acid plant. The MgO system will require water at the rate of approximately 0.002 gpm /scfm The requirement for coke is relatively low, and magnesium oxide is the major remaining input constituent. It is expected that this system can also provide a control well over 98 percent for the reverberatory furnace. Furthermore, product flexibility is obtained because the concentrated steam can be used to make liquid SO_2, sulfuric acid, or sulfur.

5.10.5 CITRATE SYSTEM

If the citrate system (Section 5.5) is used as a concentration system only, there has been sufficient experience with metallurgical gases to indicate that it can be operated with reverberatory furnace gases. The concentrated SO_2 can be driven off and used to produce either liquid SO_2 or sulfuric acid. Reduction to sulfur may be possible but additional development will still be required.

As the feed SO_2 concentration decreases, the quantity of stripping steam required increases. However, this is low pressure, generally considered, waste steam. Typical steam consumption for combustion gases of 0.3 percent SO_2 at 35°C and 90 percent recovery is 7 to 8 tons steam per ton of SO_2. In comparison, this reduces to 0.5 tons of steam per ton of SO_2 for gases of 5 percent SO_2.

The sulfite oxidation rate is very low with this system -- 0.1 percent as absorbed SO_2.

5.10.6 AMMONIA SYSTEM

The ammonia system, which produces ammonium sulfate as well as a concentrated SO_2 offgas, has been used successfully on reverberatory furnace offgases. The major problem with this system is that a use must be obtained for the ammonium sulfate product which is a fertilizer that is not currently in great demand. In addition, a source of ammonia is required. It does, however, represent proven technology.

5.10.7 WELLMAN-LORD SYSTEM

With the Wellman-Lord system, as the inlet SO_2 concentration in the flue gas decreases, the required amount of heating steam and cooling water increases. As the concentration of oxygen increases, the size of the first treatment section and the chemical makeup requirement will increase. Approximately 1-1/2 to 3 percent of the SO_2 in the flue gas entering the absorber will be oxidized depending on oxygen availability.

Since this system has not been used on reverberatory furnace offgas, it is unlikely that it would be selected unless it can show considerable economic advantages or actual operating data even though it has had extensive experience at low SO_2 gas concentrations in the utility industry.

5.10.8 COAL REDUCTION

The only system that appears to have sufficient positive experience is the one used at Trail, British Columbia by Cominco. This system has had 7 years of operating experience using concentrated SO_2 gas obtained from their ammonia concentration system using roaster offgases.

The recent experience with the FW-BF Scholtz station dry absorption system producing sulfur would indicate that additional development work is required.

The FW-BF process is an adsorption process and indicates the greatest efficiency with low concentration gases.

Coal reduction processes used by Cominco and as well as Boliden process at the Ronnskar smelter in Sweden used relatively high concentrations of SO_2. The Boliden process used 11 percent SO_2 gas, and the Cominco process used 100 percent SO_2 gas. Thus, experience indicates that it is necessary to provide a concentration system before the coal reduction to sulfur process can be used for reverberatory furnace offgases. However, the low limit of SO_2 concentration for efficient reduction has not been determined.

If a choice were required to either make sulfuric acid or sulfur, the production cost of the acid would be less than that of sulfur. However, if the acid could not be disposed of either externally or by use internally, then the additional process of converting to sulfur would appear the better approach. In other words, if it was necessary to neutralize the acid, consideration, particularly on a long term basis, should be given to reducing the SO_2 to sulfur with its considerably easier storage requirements (refer to Section 5.11).

Coal can also be considered as the source of a gaseous reductant, presumably CO within the process. Thus, the alternative is also present of producing gas from coal in an independent process and then using this gas as the reducing agent in a separate system.

The additional complexity is obvious, but the more efficient gaseous reactions could ensure direct reduction of the low concentration reverberatory furnace gases.

5.11 SO_2 CONTROL SYSTEM PRODUCT PROCESSING AND DISPOSAL

5.11.1 INTRODUCTION AND SUMMARY

As mentioned previously, the three major products that can be produced from SO_2 control systems are sulfuric acid, liquid sulfur dioxide, or elemental sulfur. Sulfuric acid concentration has been standardized as either 93 or 98 percent, although various other grades are produced.

The major market for sulfuric acid is restricted to the 93 percent and above concentrations. However, to produce phosphate-type fertilizers, 60 to 70 percent acid strength can be used. The shipping problem, as previously discussed, will of course minimize the use of this concentration unless the acid can be produced very close to the point of use. Sulfur trioxide dissolves in sulfuric acid in all proportions forming fuming sulfuric acid, often called oleum, which is sold on the basis of percent SO_3 content.

Sulfur dioxide may be liquefied by the simple process of using refrigeration and maintaining it under pressure. It can be shipped much greater distances and is a more storable product than sulfuric acid. While the market for liquid sulfur dioxide is limited, available supplies of liquid SO_2 can be used to reduce the size of smelter sulfuric acid plants reducing their capital and operating costs.

Gypsum produced by the lime/limestone system can be used either in wallboard cement or "thrown away." It is a stable product and can be placed on the ground or settled out in ponds if proper environmental control procedures are followed.

The use of ammonia for absorption and production of ammonium sulfate fertilizer as well as a concentrated steam of SO_2 has been commercially demonstrated by Cominco. However, the demand for ammonium sulfate as a fertilizer is not as great as for phosphate fertilizer primarily because of the latter's capability for flexible mixes and potential for higher concentrations of nitrogen. Also, ammonia requires fuel to produce so its cost can be expected to be related to the energy problem.

Sulfuric acid can be expected to be the major SO_2 control system product produced by copper smelters in the U.S. As long as an economic market is available for each copper producer, either externally or for internal use, systems producing this product can be used. Where acid disposal must depend on neutralization, systems producing a gypsum product become attractive because of lower capital and operating costs. In addition, gypsum can be stored conveniently in open piles because of its chemical and physical stability. Sulfur has the same storeability characteristics as gypsum, but requires fuels for production. Its potential U.S. marketability can be expected to be greater in the U.S. than gypsum.

5.11.2 GYPSUM

As indicated in Section 5.2, the lime/limestone system used at the Onahama smelter produces gypsum for sale to wallboard manufacturers. This requires that the system be operated under the conditions where the crystal size is closely controlled. Large bulky crystals are desired to minimize water adherence and also to increase the strength of the wallboard.

Presently native mined gypsum is used by wallboard manufacturers in the U.S. In 1972, U.S. gypsum producers mined 12,328,000 ton while 7,718,000 ton were imported primarily from Nova Scotia, Canada. Because of the low cost of water transportation, most imported material was shipped by water to users on the Atlantic, Pacific, and Gulf coasts. In the same year, 20,076,865 ton of gypsum were used in the U.S., and 14,205,000 ton of this or 71 percent was used in wallboard manufacturing. In addition, gypsum was used in agriculture as a soil additive, as a retarder in cement, and as a paint pigment.

A large percentage of the eastern gypsum markets use imported material from Nova Scotia. The wallboard markets in the midwest are supplied by native gypsum from nearby mines.

Western gypsum was mined in Arizona, California, Nevada, Utah, Iowa, Oklahoma, and Texas.[109] If it were produced by the smelters, there would be direct competition. If the gypsum could be sold instead of treated as a throwaway product the return would be a gain for the smelters. Thus, the sale price of Western-mined gypsum and its shipping cost would be the controlling factor. With the wide availability of gypsum and additional byproduct production from the chemical industry and powerplants, it appears that only special localized situations would allow smelter sales.

Gypsum has advantages over calcium sulfite for land filling and discarding. Gypsum can be grown into fairly large crystals (50 to 300 microns), and moisture content of the centrifuge discharge can be made as low as 10 percent. On the other hand, the crystal of calcium sulfite is normally very small (1 to 10 microns), the centrifuge discharge contains about 60 percent moisture and is similiar to paste. Thus, the calcium sulfite may not suit land filling because of the high moisture which is not easily removed, while gypsum would be useful. Furthermore, calcium sulfite has some potential for consuming oxygen in ambient water. When gypsum is discharged in a slurry form to a waste pond, it precipitates much more eaily in small volumes than does calcium sulfite, thus reducing the required pond size. In the case of truck transportation, gypsum can be handled with great ease.

5.11.3 SULFUR/SULFURIC ACID

5.11.3.1 Overview

Approximately 90 percent of the sulfur consumed is in the form of sulfuric acid. In reviewing the potential supply and demand situation, this close relationship necessitates simultaneous consideration of both materials.

Sulfuric acid has been established in industry as the lowest cost and most versatile of the mineral acids for which there is no satisfactory substitute for most applications. This, in turn, makes sulfur one of the most important of the industrial raw materials. The consumption of sulfuric acid is frequently considered proportional to the gross national product of any nation.

Sulfuric acid is widely sold in the form of various solutions of H_2SO_4 in water or of SO_3 in H_2SO_4.[110] The latter, called oleums, are marketed on the basis of the percentage of SO_3 present; 20 percent oleum means that, in 100 lb, there are 20 lb of SO_3 and 80 lb of H_2SO_4. This 20 percent oleum, if diluted with water to make H_2SO_4, would furnish 104.5 lb. For convenience, now grown into an established custom, the ordinary solutions of sulfuric acid and water, up to 93 percent, are sold according to their specific gravity, or their Baumé degree. Table 5-6 illustrates the sulfuric acids of commerce. The usual temperature to which specific gravity, or Baumé (Bé), is referred is 60°F for sulfuric acids. The specific gravity of sulfuric acid increases gradually to 1.841 at 60°F for 98 percent sulfuric acid, after which it decreases to 1.835 at 60°F for 100 percent acid. Consequently, in this upper range, i.e., above 95 percent, the strengths are determined by other means, such as electrical conductivities, titrations, or temperature rises. For some of the medium-range oleums, however, specific gravity is used.

Table 5-6. COMMERCIAL STRENGTHS OF SULFURIC ACID (60° F)

For oleums, % means free SO_3	Degrees Bé, 60°F,or 15.6°C	Specific gravity, 60°F, or 15.6°C	Sulfuric acid, %
Battery acid	29.0	1.250	33.33
Chamber acid, fertilizer acid, 50 Be acid	50	1.526	62.18
Glover or tower acid, 60 Be acid	60	1.706	77.67
Oil of vitriol (OV), concentrated acid, 66	66	1.835	93.19
96% acid	--	1.841	98.0
100% H_2SO_4	--	1.835	100.0
20% oleum, 104.5 acid	--	1.915	104.50
40% oleum, 109 acid	--	1.983	109.0
66% oleum	--	1.992	114.6

The normal strengths of commercial oleums fall into three categories: 10 to 35 percent free sulfur trioxide, 40 percent free sulfur trioxide, and 60 or 65 percent free sulfur trioxide. The 20 to 35 percent grades can readily be produced in a single absorption tower, whereas 40 percent oleum generally requires two absorption towers in series. Oleum containing 60 to 65 percent free sulfur trioxide must be made by distilling SO_3 gas out of 20 to 35 percent oleum, condensing the 100 percent SO_3, and then mixing it with additional 20 to 35 percent oleum. The freezing point of 35 percent oleum is about 80°F, and for 40 percent oleum, about 94°F; consequently, small amounts of nitric acid are sometimes added to these grades to inhibit freezing during winter shipment.

Fertilizer manufacture is the greatest single use of sulfuric acid. About a dozen different grades are supplied, each with a particular use. Grades of 53° to 56° Bé or stronger are employed in normal superphosphate manufacture. The 60° Bé grade is used for sulfates of ammonia, copper (bluestone), aluminum (alum), magnesium (Epsom salts), zinc, iron (copperas),; mineral acids; organic acids, such as citric, oxalic, acetic, and tartaric; pickling iron and steel before galvanizing and tinning; refining and producing of heavy metals; electroplating; and processing of sugar, starch, and syrup. The 66° to 66.2° Bé grades are utilized in purification of petroleum products; preparation of titanium dioxide; alkylation of isobutane; manufacture of many nitrogen chemicals; synthesis of phenol; recovery of fatty acids in soap manufacture; and manufacture of phosphoric acid and triple superphosphate. Oleums are needed for petroleum, nitrocellulose, nitroglycerin, TNT, and dye manufacture, and for fortifying weaker acids. There are many other uses, as can be attested to by the fact that few chemical products are made into which the manufacture of sulfuric acid does not enter in some way or other.

The contact process is used to produce 93 percent to 100 percent acids and the various oleums. Most 66° Bé and 60° Bé acids are obtained by dilution.

Sulfur is obtained by melting with hot water in underground deposits and pumping to the surface (Frasch process) or by various processes from SO_2 or H_2S with the source of the latter two from sulfide ores or petroleum processing. It is shipped as a liquid in special rail tank cars, the availability of which sometimes effects the supply situation.

Sulfur in its various forms is produced worldwide with no one country being a predominant producer or supplier to world markets. In 1975, world production amounted to 52 million tons.[111] The United States is not only the largest producer of sulfur in the world, but also consumes more than any other country. In 1975, production totaled 11.26 million tons and consumption 10.6 million tons.

The major problem facing the domestic sulfur-producing industry, and to a lesser extent in the rest of the world, is a very probable basic change in the major sources of sulfur supply. Fundamentally, this will be brought about by the necessity for the removal of sulfur from solid, liquid,and gaseous effluents or wastes for the protection of the environment. Secondarily, it will be influenced by the forceable exhaustion of cheap sources of noncombined sulfur. U.S. Bureau of Mines predicts that the enforced production of coproduct sulfur for environmental reasons will completely reverse the present supply pattern.[112] Although in 1975, 64 percent of current domestic supplies of sulfur were obtained from noncombined sulfur deposits (Frasch type), the long-range expectation is that 83 percent will be obtained from coproduct sources regardless of costs.[113] Additionally, these later sources may provide an overabundance of supply, at least regionally if not nationally (particularly in the form of sulfuric acid). The latter condition will satisfy the needs of the consumers, both in terms of amounts and price levels. However, it will create problems for both primary and coproduct producers.

The nonsulfur industries affected by environmental necessities require the development of technologies that will permit them to cover the capital and operating costs of coproduct sulfur recovery at cost levels that will be competitive with other sources. If such technology is not available, the industries will be forced to absorb at least a portion of the cost of coproduct sulfur production into the cost of their prime product. This added cost will be passed on to the consumers of their basic products in the form of higher prices.

A detailed discussion of the general sulfur/sulfuric acid sources present uses, new uses, present product and consumption, future market projection costs and pricing are included in Appendix X.

5.11.3.2 Smelter Sulfur/Sulfuric Acid Market

Acid plants have been used conventionally to control SO_2 from the primary nonferrous smelters. Presently, only streams containing high enough SO_2 concentration for autogenous conversion to sulfuric acid are being treated. Streams containing low SO_2 concentrations are discharged directly to the atmosphere. But with the increasingly stringent emission regulations, the smelters might be forced to control SO_2 from the weak streams. The smelters in that case would have two alternatives: (1) either to use a regenerative absorption system to produce elemental sulfur, liquid SO_2, or sulfuric acid; or (2) to install a nonregenerative absorption system, producing a stable throwaway product which could be disposed of without any adverse effect to the environment.

The quantity of sulfuric acid that a smelter can sell is dependent on the other supplies of sulfur/sulfuric acid and costs, distance of the smelter from the markets, etc (Appendix X). It is obvious that a thorough marketing study for smelter sulfuric acid can only be done by knowing the demand for sulfuric acid in various regions of the country, the cost of making sulfuric acid in a conventional acid plant using Frasch or recovered sulfur, the distance of the markets from the smelters to determine the cost of transporting the acid, etc. These factors can also change with time.

Determination of the quantitites of smelter acid that could find a market, and the net return that the smelter could expect from this acid, are very complex. It is related to the distance of the smelter from the potential markets and the cost of sulfur. For a given sulfuric acid demand in a particular region, the quantity of smelter acid that could be moved into the market is dependent on the cost of the smelter acid to the user compared to the cost of acid from conventional plants.

Table 5-7 gives the acid capacity, average acid production, and ultimate acid capacity of the nonferrous primary smelters in the U.S. Based on the available information, the annual ultimate acid capacity of the nonferrous primary smelters is more than 9.6 million tons. The annual ultimate production of the Western U.S. smelters (west of Mississippi River) is nearly 7.6 million tons. Due to the proximity of the markets to the smelters in the Eastern U.S., smelter acid could compete very favorably with the conventional acid plants producing acid with Frasch sulfur. The annual ultimate eastern smelter acid production amounts to little over 2 million tons. Due to the favorable marketing conditions for the smelter acid, it could be concluded that all the acid produced by the eastern U.S. smelters could be marketed easily.

Western U.S. sulfuric acid production from all sources in 1975 accounted for approximately 7.6 million tons or 16 percent of total U.S. capacity.[114] This is about the same quantity that the western U.S. smelters could potentially produce. So under present market conditions, the only way that the smelters can sell all their acid in the western U.S. is if they capture the entire market in this area. However, this is not possible because they will

Table 5-7. SULFURIC ACID NEAR TERM CAPACITY PRESENT PRODUCTION AND ULTIMATE CAPACITY OF U.S. NONFERROUS SMELTERS

Smelter	Near Term Capacity (ton/day)	Average Production (ton/day)	Ultimate Capacity (ton/day)
COPPER			
Asarco, Tacoma, Washington	200	120 (72)	800
Magma, San Manuel, Arizona	2400	1950 (74)	2750
Kennecott, Hayden, Arizona	950	990 (74) 365 (73) 600 (Six days in June '74)	1035
Kennecott, Mc Gill, Nevada	500	146 (75)	1260
Phelps Dodge, AJO, Arizona	750	545 (74) 105 (June 74)	576
Kennecott, Hurley, New Mexico	650	602 (74) 580 (Last five months of '74) 535 (Jan. '75) 465 (Feb. '75)	1550
Asarco, Hayden, Arizona	1008	600 (73) 360 ('73) 450 (July '73) 430 (First 10 months of '74)	1650
Phelps Dodge, Morenci, Arizona	3100	2000 (74)	2900
White Pine, Michigan	0	0 (74)	330
Phelps Dodge, Douglas, Arizona	0	0 (74)	2200
Asarco, El Paso, Texas	525	404 (74)	530
Cities Service Smelter, Copperhill, Tennessee	4010	4010 (74)	4050
Kennecott, Garfield, Utah	1400	N/A	N/A
Anaconda, Anaconda, Montana	1100	N/A	N/A
Inspiration, Miami, Arizona	1300	N/A	N/A

Table 5-7. SULFURIC ACID NEAR TERM CAPACITY PRESENT PRODUCTION AND ULTIMATE CAPACITY OF U.S. NONFERROUS SMELTERS (concluded)

Smelter	Near Term Capacity (ton/day)	Average Production (ton/day)	Ultimate Capacity (ton/day)
LEAD			
St. Joe Minerals Co., Lead Smelter, Herculaneum, Missouri	300	173 (74)	355
Asarco, E. Helena, Montana	475	N/A	448
Asarco, El Paso, Texas	280	N/A	331
Amax, Boss, Missouri	200	240 (75)	280
Asarco, Glover, Missouri	0	0 (75)	290
Bunker Hill Co., Kellog, Idaho	300	230 (75)	335
ZINC			
Asarco, Corpus Christi, Texas	225	N/A	N/A
Asarco, Columbus, Ohio	175	N/A	N/A
Asarco, Amarillo, Texas	0	0	250
National Zinc, Bartlesville, Oklahoma	275	N/A	N/A
Bunker Hill, Kellog, Idaho	650	N/A	N/A
St.Joe, Monaca, Pennsylvania	1025	N/A	N/A
New Jersey Zinc, Palmerton, Pennsylvania	500	N/A	N/A
Amax, Blackwell, Oklahoma	0	0	500

Near Term Capacity is the existing acid plant capacity or planned acid plant capacity.

Average Production is the average actual production based on the available information.

Ultimate Capacity is the ultimate quantity of acid that could be produced if all the SO_2 from the smelter is converted to acid.

N/A - Information not available

have competition from the recovered sulfur from California refineries and Canadian recovered sulfur. So the smelters in the western U.S. will have to find markets for part of their acid in the Midwest, East, and Gulf coasts. How much of this market they can capture is dependent on the acid market price, the transportation costs of the smelter acid to these markets, and the pricing of the smelter acid.

In selling byproduct sulfuric acid, the marketer must deal with potential sales resistance due to possible lower quality (impurities) and also with the need on the part of consumers for dependable acid supplies. Due to the tendency for lower quality of acid from smelters, there are a few sulfuric acid markets that may not be available to the smelter acid. But for most applications, the quality of the smelter acid can be assumed acceptable since it is used in such large quantities today, and the only remaining question is whether or not markets exist or could be developed for the increased quantities of acid that might be produced by the Western smelters.

Sulfuric acid consumers generally desire low price, high quality, and dependability. For these reasons, many large sulfuric acid consumers choose to purchase sulfur and produce sulfuric acid onsite. Heat generated when sulfur is burned can also be used for other plant processes. At $1.25 per mill Btu, byproduct steam represents an energy credit of approximately $5/ton of sulfuric acid produced.[117] For byproduct smelter acid to displace this acid it must not only be sold at less than the integrated acid producer's variable cost, but it must also compete with this energy credit on a delivered cost basis.

Sulfuric acid plants are widely scattered through the U.S. chiefly because of the bulk value of acid, difficulties of handling the acid in the bulk, and subsequent high cost of shipment as compared to elemental sulfur. Therefore,acid has been traditionally produced by sulfur-burning plants near the point of consumption in captive use. However, with the recent advent of regional imbalance in sulfuric acid supply and demand, more distant rail shipment and, to some extent, ocean transportation, has become more important.

Many existing conventional sulfuric acid plants are old and will soon need replacing.[115] Producers in this situation will possibly like the opportunity to buy abatement acid in lieu of building a new plant. Some not-so-old conventional acid plants will have to put in control systems to control the emissions from their tail gases. If the cost of byproduct smelter acid is less than the operating costs of these conventional plants, they might close down their plants and buy the smelter acid.

Smelter acid, since it would be produced nearby, could capture the entire market for acid in the mountain states. On the other hand, very little market could be captured in the southwest central region. The primary reason is that the market located along the Gulf coast is a considerable distance from most of the western smelters, and acid can be produced there at relatively low cost from Texas and Louisiana Frasch sulfur.

Acid from the smelter in Washington could find markets in Washington, California, and adjacent states. Smelters from Utah-Nevada could find markets for all of their acid in Utah, Nevada, Kansas, Missouri, and Oklahoma.[116]

Smelters located in Arizona, New Mexico, and Texas are not as well-situated to supply sulfuric acid for fertilizer manufacture. The nearest source of phosphate rock is northern Utah, Wyoming, Idaho, or Montana. The agricultural markets that could be supplied from fertilizer plants using acid from Arizona, New Mexico, and Texas smelters lie primarily in California, Arizona, and New Mexico, with a smaller market in far west Texas. However, part of this sulfuric acid for the fertilizer in this area would come from sulfur recovered from refineries in California. Another possible market that could be captured by the acid from these smelters would be the phosphate fertilizer market in Kansas and Nebraska. Fertilizer could be made in Kansas from phosphate rock from Idaho, and acid could be made from smelters in Arizona, New Mexico, and Texas. But they will be in competition with fertilizer produced in Florida from Florida phosphate rock, and acid made from Gulf coast Frasch sulfur.

Uranium ore processing and copper leaching represent two relatively bright areas in the sulfuric acid end use scheme. Copper leaching has recently become more attractive, partially because of the ready availability of byproduct sulfuric acid from smelter gases and partially because of hydrometallurgical process developments for metal recovery from ore tailings. The impetus for such research has been the need to develop technology which would satisfy the current standards of clean air legislation.

Leaching of low grade copper ores in Arizona, New Mexico, and Texas region is rapidly becoming an important use of acid. Many of the copper companies operating smelters in this region percolate weak sulfuric acid solutions through their mine dumps and wastes whose copper contents are too low to justify concentrating in a conventional mill. The solutions dissolve some of this copper which is recovered by cementation when the solutions are passed through launders full of shredded cans. A few companies are leaching higher grade ores from smaller deposits. One company is recovering anode grade copper by using solvent extraction to prepare a low iron-copper sulfate solution suitable for direct electrolysis to deposit the copper.

Smelters from Arizona, New Mexico,and Texas could also supply the acid requirements of some uranium mills in the southwest. If, as predicted by some experts, there is a shortage of sulfur in the future, it would be possible to export the recovered sulfur from California and the smelter acid could take over the domestic market.

Smelters in Idaho and Montana appear to be better located to supply sulfuric acid for the production of phosphate fertilizer.

About 16 percent of the phosphate rock mined in the U. S. comes from nearby Idaho, Montana, northern Utah, and northwestern Wyoming, and the smelters are near large and growing markets for fertilizers. The acid from this region might get some competition from Canadian recovered sulfur, but this competition could be expected to decrease as the recovered sulfur production decreases in the future. Uranium processing represents an increasing potential market for sulfuric acid produced by smelters in this region. Uranium processing is expected to increase in eastern Washington and Wyoming in the future. It is also possible for the smelters in this region to make ammonium sulfate and sell it as a fertilizer.

It is quite possible that all the smelters might not be able to sell all their acid or use it internally. If the acid markets are very far away from a smelter, the smelter acid may not be able to compete with conventional acid, owing to the very high transportation cost. But it might be possible to produce elemental sulfur and ship it to these markets. Some FGD systems described in Section 5 produce elemental sulfur. Since sulfur is the preferred product from the marketing point of view, it appears desirable to further develop the FGD systems to economically produce this product.

5.11.3.3 TVA Market Study

TVA has been conducting studies focused on elemental sulfur as well as sulfuric acid as a potential byproduct from FGD processes installed in power plants located in the states served by the inland waterway system in eastern U.S.[118] They are in the process of preparing a final report covering full assessment of markets for abatement sulfur and acid from all sources in the 48 contiguous states of the U.S. The objectives were outlined to provide general and practical information concerning the current production, distribution, use of sulfur and sulfuric acid in the U.S., and its effect on abatement products. The study indicated a potential Frasch sulfur shortage in the next 10 to 20 years.

The Frasch sulfur industry is dominated by a few large producers. The industry is concentrated, and production is centralized in a few mines located within a small region of the Texas and Louisiana Gulf Coast. The marketing system is highly organized and specialized. It has the flexibility of marketing either elemental sulfur or sulfur in the form of sulfuric acid. Most molten sulfur is shipped by water from the mines or transhipment terminals on the Texas and Louisiana Gulf Coast to the marketing terminals. Marketing terminals are strategically located either on the inland waterway system or along the east coast adjacent to ports served by deepwater vessels. From the marketing terminal, molten sulfur is transported by barge, truck, or rail directly to the point of consumption.

Capital and operating costs for mining sulfur by the Frasch process, marketing terminal storage, manufacturing acid by the contact process with storage, and controlling acid plant tail gas emissions were calculated by TVA to determine the competitive costs of sulfur and acid production.

By the use of power plant design and operating data provided in the U.S. Federal Power Commission Form 67, a data bank was constructed by TVA to accommodate key operating parameters for all power plants in the U.S. Parameters such as fuel type, sulfur in fuel, boiler heat rate, fuel consumption, on-stream time, age of plant, etc., are vital. Using these data, possible output of byproduct can be calculated for each power plant - given the level of SO_2 control designated by March 1975 SIP standards.[119]

With the large data base available from FPC Form 67, it was possible for TVA to create a more accurate screen to center on the most promising power plant candidates for abatement byproduct production. Earlier work by TVA for EPA contains well defined investment and operating cost estimates of the five leading FGD systems based on key power plant design and operating parameters.[120] In the EPA-TVA cost report, two of the processes (the magnesia slurry scrubbing-regeneration process producing 98 percent sulfuric acid, and the sodium solution-SO_2 reduction process producing elemental sulfur) produce saleable byproducts. The costs of these processes can be compared with those of the throwaway limestone slurry scrubbing process in deciding what scrubbing strategy is to be adopted for each boiler or plant where appropriate.

For boiler operators who do not select an alternative strategy, such as clean fuel substitution, the question remains as to whether they would produce (1) sulfuric acid, (2) sulfur, or (3) a throwaway sludge. While the sulfur alternative was modeled by TVA, production costs with current technology were high enough that this alternative did not require a computer run to conclude that sulfur would not be chosen over acid at any boiler. The throwaway sludge alternative was analyzed in detail since it is the lowest cost scrubbing method. In this case marketing revenue would have to exceed the cost differential for a given boiler before acid production would be selected.

An extremely important component of the TVA model is the transportation data base for computing accurate shipping costs for sulfur and sulfuric acid. Since shipping cost is an essential element in the price of acid and sulfur, a great deal of creative and complex effort was required to derive usable values for the entire U.S.

As a part of the model design, it was assumed by TVA that the sulfuric acid market can be simulated as though all consumption occured at sulfuric acid plants, and that acid-producing firms would close these plants and buy abatement acid if acid prices were below their expected long-run average total cost. It was also assumed that steam plants would produce sulfuric acid or sulfur if that were the least costly alternative for meeting clean air requirements. Long-run competitive equilibrium market conditions can be simulated by minimizing the cost to both the sulfuric acid and power industries. In this framework, power plants were assumed free to produce or not produce sulfur or sulfuric acid and to sell to any sulfuric acid plant in competition with other power plants. Likewise, the sulfuric acid plants were assumed free to continue buying sulfur from traditional sources or from power plants, and free to buy acid in lieu of production subject to competition in their respective industries.

The TVA model considers the total cost of both the sulfuric acid and power industries and chooses the set of alternatives that minimize the total cost. Sulfuric acid producers are given a choice of continuing production or buying acid from steam plants. Steam plants not meeting SIP are given the choice of (1) selecting a clean fuel strategy, (2) selecting a calcium sludge scrubbing technology, or (3) selecting a sulfuric acid or sulfur-producing scrubbing technology. In the latter case, product would then be available to supply sulfuric acid plants if they choose to buy it. The mix of abatement strategies and marketing patterns resulting in the lowest possible cost to the combined industries is said to be optimal.

At a very high supply cost from power plant producers, only a few acid plants would be better off buying rather than producing sulfuric acid. These plants tend to be old, low-volume producers far from sulfur supplies. As supply cost declines, very high-cost producers disappear rapidly and the demand curve for abatement acid flattens. At low supply costs from power plants, all but the largest, most modern acid plants located near sulfur supplies would buy rather than continue production. Small quantities of abatement acid could then be marketed at high value but as the supply increases the value declines.

It was concluded in the TVA study that when sulfur value is $60/ton f.o.b. Port Sulfur, there would be no power plant production without regulations for emission control. As plants are forced to take some action, the cost of alternative controls can be considered as a credit to recovery processes and provides the basis for assigning a sulfuric acid market adjustment value. The preliminary results from the study indicate that a significant amount of byproduct sulfuric acid could be moved within the present market structure at a sales value high enough to make sulfuric acid FGD process competitive with throwaway sludge systems.[121]

The possibility of applying the TVA computer program to the smelter acid marketing study appears promising and will be pursued in the near future.[122]

5.11.4 LIQUID SO_2

The demand for liquid SO_2 in the U.S. is very limited. The current U.S. liquid SO_2 capacity is approximately 177,000 ton/yr.[123] The single largest use for SO_2 is in the production of sodium hydrosulfite which in turn is used as a bleaching agent in the production of textiles, paper, and clay. The use of SO_2 in pulp and paper manufacture is dwindling due to more stringent controls on SO_2 emissions. Other uses for liquid SO_2, including refining and food processing, are expected to offset the lower demand in pulp and paper. The result will be that liquid SO_2 demand is expected to increase at an annual rate of approximately 4 to 5 percent during the next 5 years.[124]

Owing to the relatively high price per unit weight of liquid SO_2, unlike sulfuric acid, it can be shipped long distances to serve various markets. Due to the stable markets, the supply/demand situation for U.S. liquid SO_2 is in balance. An increase or decrease in production of 10,000 to 20,000 ton/yr, representating 6 to 12 percent of estimated 1975 consumption, would significantly disrupt the market for this chemical.[125]

Since the liquid SO_2 market in the U.S. is very small and is already in balance, the possibility of a nonferrous smelter putting in a system to produce liquid SO_2 exclusively for sale is not likely. However, liquid SO_2 can be used to smooth out the feed to the acid plant to compensate for the smelter offgas fluctuations. This technique can also be used to reduce the size and cost of acid plants installed at the smelters.

5.11.5 ACID NEUTRALIZATION

5.11.5.1 General

In the copper industry, almost all of the sulfur recovered is in the form of concentrated sulfuric acid. Presently, all the sulfuric acid produced by copper smelters is either used internally or is marketed. In case the copper smelters are unable to market their sulfuric acid, storage facilities and/or acid disposal facilities must be available. This situation could occur if the smelter is located far from the acid markets and are unable to consume the acid internally. Before installing an acid neutralization facility at any specific smelter, a detailed engineering, marketing, and economic analysis would be performed to ensure that acid could not be used for additional copper production through leaching, sulfuric acid based chemical products, gypsum products, and production of elemental sulfur.

There are generally two types of neutralization processes for sulfuric acid disposal, so-called "wet" and "dry". In the "wet" process, neutralization reaction takes place in dilute acid-water solution and produces a calcium sulfate slurry for disposal. The neutralization reaction in the "dry" process takes place directly between concentrated sulfuric acid and limestone producing a plastic mass that eventually turns into a dry solid for disposal.

Limestone is usually the cheapest chemical for the neutralization of acid, although using lime would permit smaller reactors with less retention time owing to the higher reactivity of lime. But lime is fairly expensive compared to limestone. Limestones are carbonate rocks or fossils composed principally of calcium carbonate or combinations of calcium and magnesium carbonate with various impurities. Hill and Wilmouth report that limestones containing magnesium react more slowly than those composed of calcium carbonate.[126] Also, neutralization rate has been shown to increase with increasing fineness of limestone, the limit of this being economic because the cost of grinding increases sharply as particle size decreases. If appreciable amounts of magnesium are present in the limestone used for neutralizing acid, leaching of the magnesium salts from the disposed waste could become a problem.

The limestone source is of crucial importance in the neutralization reaction. Large differences in reactivity can be experienced depending upon the type of limestone used. It is, therefore, very important that the actual limestone to be used in the commercial process be the basis of limestone neutralization studies.

Davies et al of Kennecott Copper Corp., briefly describe the "dry" and "wet" acid neutralization processes.[127] The "wet" process causes the neutralization reaction to occur in dilute acid-water solution and produces a calcium sulfate slurry for disposal. The neutralization reaction in the "dry" process occurs directly between concentrated sulfuric acid and limestone producing a plastic mass that eventually turns into a dry solid for disposal.

Little direct experience exists for disposal of concentrated sulfuric acid, except by dilution. There are, however, excellent process analogies available in the fertilizer industry where wet process phosphoric acid is made by reacting phosphate rock with concentrated sulfuric acid in a slurry system, and normal superphosphate is made on a dry basis by the same reactants in a pug mill or TVA cone. Much of this technology is therefore directly adaptable.

A most important factor in the design of neutralization facilities is the disposal method for the calcium sulfate waste produced. Transport problems, effect on water hardness, effect of dissolved salts on ground water, effect on tailings pond, dusting problems, water requirements, piping scaling, and dry material stability must all be considered.

5.11.5.2 Dry Process

The process flow diagram for acid neutralization by the "dry" process is given in Figure 5-20. Fundamentally, the dry process is the reaction of ground limestone and acid in a "blunger", paddle mixer, or a pug mill. This type of equipment is used to manufacture normal superphosphate fertilizer by reacting sulfuric acid with ground phosphate rock. The pug mill produces a soupy, sticky mass which requires aging to complete the reaction. Aging occurs on a wide slow-moving conveyor. At the end of this conveyor, a solid continous mass exists, more or less dry, which must be broken up into granular fragments for subsequent handling.

This process produces principally anhydrite, $CaSO_4$, and hemihydrate, $CaSO_4 \cdot 1/2H_2O$; the reaction heat is sufficient to heat the end products beyond the point where gypsum ($CaSO_4 \cdot 2H_2O$) dehydrates. The reaction products will hydrate, at least partially, to gypsum or to hemihydrate upon exposure to atmospheric moisture.

Crushed mine limestone is stored in a limestone silo which feeds a grinding mill. The milling system is equipped for closed circuit grinding with provision for dust collection in a baghouse. The ground limestone (80 percent minus 100 mesh) is fed to the pug mill at a controlled rate through a weigh feeder. The acid to be neutralized is also fed to the pug mill at a controlled rate through an acid flowmeter. Since the reaction in the pug mill is exothermic, fresh water is added to the reactor to control the temperature. Fresh water addition also provides the output product with proper consistency. Control of the process is by visual inspection of the pug mill mass and adjustment of the acid flow to suit the operator's experience.

The reacted mass from the pug mill is discharged onto a slow moving conveyor and the mass cures. The conveyor carries the mass to a cutter which cuts the solid mass to small pieces to facilitate its handling. This cut mass goes to a mobile haulage station for final dry disposal. The gases from the pug mill are scrubbed before being discharged to the atmosphere.

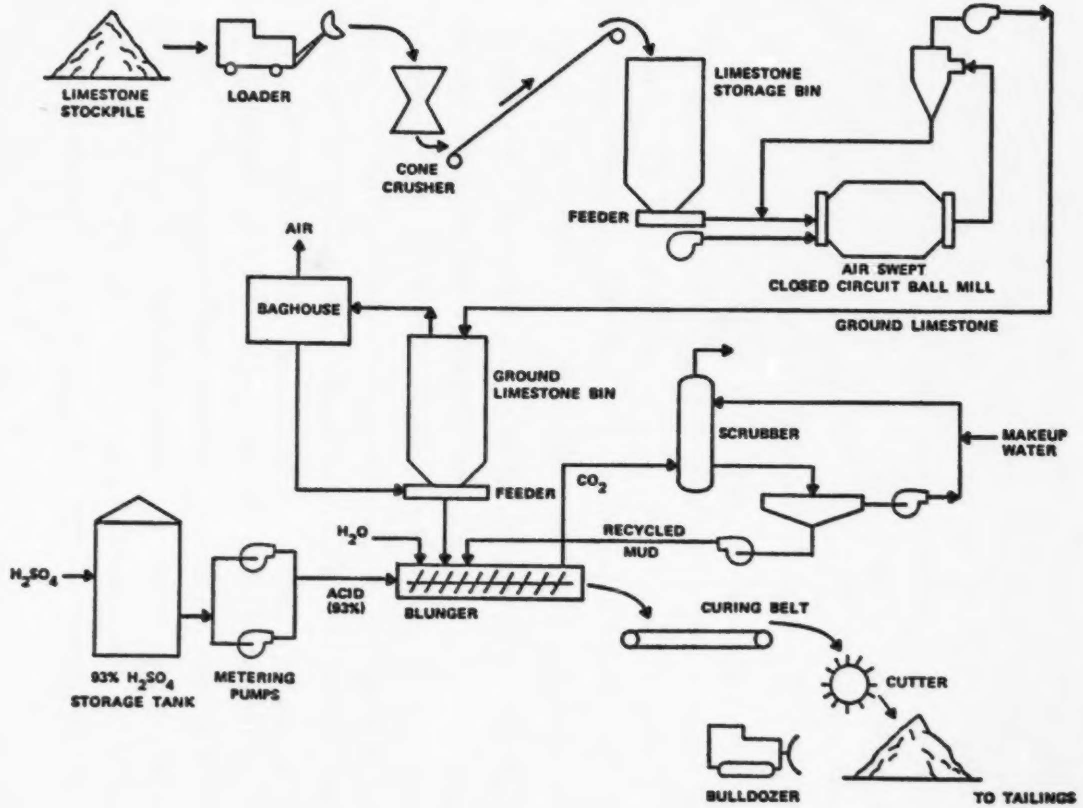

LIMESTONE STOCKPILE
LOADER
CONE CRUSHER
LIMESTONE STORAGE BIN
FEEDER
AIR SWEPT CLOSED CIRCUIT BALL MILL
GROUND LIMESTONE
AIR
BAGHOUSE
GROUND LIMESTONE BIN
FEEDER
SCRUBBER
MAKEUP WATER
CO_2
H_2O
RECYCLED MUD
H_2SO_4
ACID (93%)
BLUNGER
93% H_2SO_4 STORAGE TANK
METERING PUMPS
CURING BELT
CUTTER
BULLDOZER
TO TAILINGS

Figure 5-20. Sulfuric Acid Neutralization - Dry Process

5.11.5.3 Wet Process

The process flow diagram for acid neutralization by the "wet" process is given in Figure 5-21.

Crushed limestone from the limestone silo is fed to a wet grinding ball mill where limestone is ground to a slurry (80 percent minus 100 mesh particle size). This slurry is then pumped to the neutralizing reactor station which consists of two or more reactors operating in series.

Acid is pumped to the first reactor at a controlled rate. The operator controls the acid rate by remote control of pump speed to maintain the proper sulfate concentration (0.2 to 0.5 percent) in the outlet of the second or last reactor. A constant recycle of slurry (approximately 50 percent recycle) is maintained to control scaling and to promote gypsum crystal growth.

Reactor temperature is controlled to 71°C (160°F) by adding fresh water and evaporative cooled reclaim water recycled from the disposal pond. The neutralization reaction is quite exothermic (it generates approximately 725 Btu/lb of H_2SO_4 neutralized) and thus requires cooling or large water excess to control the temperature. The reactor system is designed to provide 2 hours retention time.

Waste gypsum slurry is discharged to the tailing pond by gravity flow. The tailing pond provides area for cooling by surface evaporation and for ponding of water. In the design,it has been assumed that the tailing will retain 40 percent moisture, and the remaining water is recycled to the reactor system.

5.11.5.4 Cost Considerations

Both wet and dry acid neutralization processes are technically feasible. However, the choice of neutralization process must be based on the particular circumstances existing at each plant location. The cost of limestone, as well as the limestone grind required for

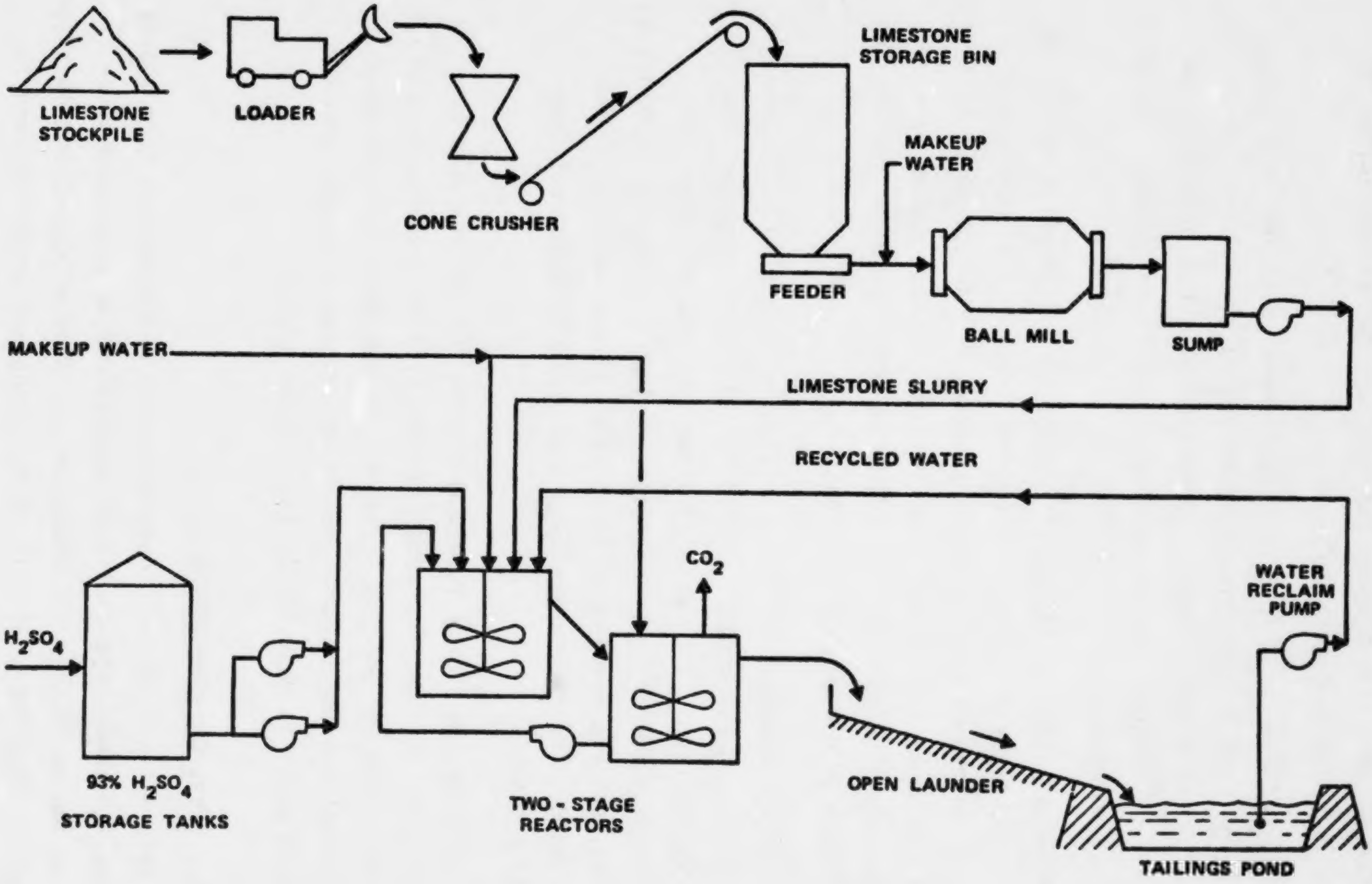

LIMESTONE STOCKPILE
LOADER
CONE CRUSHER
LIMESTONE STORAGE BIN
MAKEUP WATER
FEEDER
BALL MILL
SUMP
MAKEUP WATER
LIMESTONE SLURRY
RECYCLED WATER
H_2SO_4
CO_2
WATER RECLAIM PUMP
93% H_2SO_4 STORAGE TANKS
TWO - STAGE REACTORS
OPEN LAUNDER
TAILINGS POND

Figure 5-21. Sulfuric Acid Neutralization - Wet Process

efficient reaction, are sensitive cost parameters and require careful evaluation for each application. Final costs will be influenced by limestone transportation, acid transportation, plant site and disposal area land availability, waste product transportation to the disposal site, and utilities availability. Table 5-8 gives the wet and dry H_2SO_4 - limestone neutralization process evaluation summary given by Davies et al.[128]

Other than direct process-related capital and operating costs, the decision rests on the disposal method for the byproduct calcium sulfate, management of the disposed byproduct from the environmental and cost viewpoint, process reliability and ease of operation, limestone source and reserves, and water restrictions.

Full engineering and economic analysis of both the wet and dry process under conditions that exist at any given plant location must be undertaken to determine true overall capital and operating costs. A cost advantage of one process over the other can emerge if, for example, limestone costs are high, or pond disposal management is inordinately expensive.

5.12 SUMMARY

Two processing systems emerge as feasible for reverberatory SO_2 offgas control. The first system would eliminate the SO_2 through production of a throwaway product. The other would include systems designed to upgrade the weak SO_2 gas to one amenable either directly or by blending with converter and/or multihearth roaster offgases for conversion to sulfur acid. Thus, for the latter approaches, offgases processed in a sulfuric acid plant will limit SO_2 emissions to 650 ppm for a double contact acid plant, or 2,600 ppm for a single contact sulfuric acid plant.

The background information developed for the new source performance standards for primary copper smelters investigated scrubbing systems capable of handling weak stream SO_2 offgases.[129] During the past 40 years, over 50 process schemes utilizing various types of absorbents as scrubbing media have been investiga-

Table 5-8. WET AND DRY H_2SO_4 LIMESTONE NEUTRALIZATION PROCESS EVALUATION SUMMARY

	Wet Process	Dry Process
Capital Cost (600 T/D, 93% H_2SO_4)	$4,700,000	$4,200,000
Operating Cost per ton 93% H_2SO_4 including		
Limestone @ $1/ton delivered	$ 7.66	$ 7.95
Cost per ton of sulfur neutralized	$25.22	$26.15
Process Status	Developed	Developed
Process Reliability	Good	Fair - good
Process Operability	Good - easy control	Good - somewhat more difficult control and maintenance
Gypsum Disposal Method	Gypsum pond	Dry pile or gypsum pond
Water Consumption	324-540 gal/ton of H_2SO_4 with reclaim; 1,830 gal/ton of H_2SO_4 without reclaim	83-128 gal/ton H_2SO_4
Environmental Considerations	Runoff and groundwater control required, some dusting from pond walls. Pond water will be slightly acid for separate gypsum pond case.	Rain runoff control required, dust control.
Effect on Concentrator	None if separate pond. Dissolved salts buildup in concentrator water if gypsum is sent to main plant tailings pond.	None unless disposal of in main plant tailings pond, then same as wet process.

ted primarily for the utility industry. This has been on a bench-scale, pilot-plant, or prototype basis, in an effort to perfect the optimum control for low concentrations of SO_2 in process offgases. As a result, it was concluded that four scrubbing systems appeared viable as control methods for low concentrations of SO_2 based on transfer technology or actual use in the copper industry.[130] These systems included:

1. Calcium-based scrubbing systems (lime/limestone)
2. Dimethylaniline (DMA) scrubbing systems
3. Ammonia scrubbing systems
4. Sodium sulfite - bisulfite scrubbing

Of the above, only the calcium-based and ammonia scrubbing systems seem applicable to weak stream SO_2 offgases from reverberatory furnaces. The DMA scrubbing system was considered viable only for SO_2 concentrations in the range of 4 to 10 percent as a result of the poor absorption characteristics of DMA below 2 percent. It has not been demonstrated that the sodium sulfite - bisulfite scrubbing system can be operated to control smelter offgases without excessive absorbent sulfate conversion resulting in a required large purge stream and, consequently, high costs because of the relatively high oxygen and SO_3 content of smelter gases.

Further review of the literature indicated the following systems have been used to control SO_2 in reverberatory furnace offgases:[131]

1. Lime/limestone scrubbing system
2. Magnesium oxide concentration system
3. Citrate concentration system
4. Cominco ammonia scrubbing system

Coal reduction to sulfur has also been demonstrated with metallurgical gases.

The lime/limestone system resulting in a "throwaway" product, gypsum, is currently in operation on reverberatory furnaces at the Onahama Smelter in Japan, as well as for many utility offgas streams. The SO_2 concentration to this system is currently 2.5 to 2.8 percent. Lower SO_2 concentrations will actually allow this system to become more efficient in terms of sulfur capture. However, if this lower concentration is obtained by dilution, then the size of the gas handling equipment must be enlarged. If the reduced concentration is obtained by reducing sulfur elimination in the furnace, then this advantage can be efficiently exploited.

It is expected that the lime/limestone system can operate satisfactorily with current reverberatory furnace SO_2 concentrations resulting from a calcine feed. Additionally, with a lower quantity of SO_2 to be treated, there will be a lower quantity of solid waste which will minimize handling and disposal.

The MgO system has also been satisfactorily operated on reverberatory offgas at the Onahama Smelter in Japan, as well as some prototype work on utilities. This system produced a concentrated gas stream of 10 to 13 percent SO_2, which could be processed directly in a sulfuric acid plant or blended with those offgases from multihearth roasters and converters, and subsequently processed in a sulfuric acid plant.

The citrate system has been satisfactorily operated at the Boliden AB Ronnskarverken Smelter at Skelleftehamm, Sweden on metallurgical gases. The Bureau of Mines has also obtained promising data on the citrate absorption portion of a larger sulfur producing system. The citrate process can also be used for gases with varying concentrations of SO_2, such as tail gases from metallurgical and chemical processes as well as from power plant flue gases.

The Cominco ammonia system, which produces ammonium sulfate as well as concentrated SO_2 offgas, has been successfully used on reverberatory furnace offgases. A use must be obtained, however, for the ammonium sulfate product not currently in great demand. In addition, a source of ammonia is required. It has been reported that secondary pollution from ammonia plume formation is a serious problem but pilot plant tests which are now being followed by full scale plant construction indicate full scale solution will be achieved in 1981.

The Smelter Control Research Association's (SCRA) recent studies using ammonia double alkali system indicated some potential for application of this approach.[132] The major question still present concerns economically obtaining ammonia, as well as the fact that this system has not been used on a full-scale application.

With the Wellman-Lord system, as the inlet SO_2 concentration in the flue gas decreases, the required amount of heating steam and cooling water increases. As the concentration of oxygen increases, the size of the first treatment section and the chemical makeup requirements will increase. Although it has had extensive experience at low SO_2 gas concentrations in the utility industry, it has not been used on reverberatory furnace offgas or any other metallurgical gas.

The coal reduction systems used at Cominco were fed relatively high SO_2 concentrations. The lower limit for SO_2 concentration for efficient reduction has not been determined. Also, the production cost of sulfuric acid is less than that of sulfur, so only in those cases where the acid can not be disposed would this system seem attractive.

The operating experience with the MgO, lime/limestone, ammonia and citrate systems on copper smelter reverberatory furnace offgases indicates that from a technical standpoint, they are available to control SO_2 emissions. However, the ammonia system might pose a potential adverse ammonia availability problem as noted above. Thus, four FGD systems: lime/limestone, MgO, ammonia and citrate emerge as applicable for handling weak stream SO_2 offgases.

SECTION 6

APPLICATION TO NEW SMELTERS

6.1 PLANT EMISSION DESULFURIZATION SCENARIOS

6.1.1 INTRODUCTION

A green field smelter using roasters, or no roasters with a reverberatory furnace and converters was used as the basic system to apply SO_2 control systems along with operating modifications to provide optimum collection and capture. A series of 60 different scenarios were generated and are summarized in Tables 6-4, 6-5, and 6-6.

Oxygen enrichment, leakage control and continuous charging are typical operating techniques considered. Flue gas desulfurization or neutralization systems were used and blending of weak and rich SO_2 streams were incorporated as applicable.

6.1.2 BACKGROUND ASSUMPTIONS

One technique for upgrading offgases to allow SO_2 processing in a sulfuric acid plant is to blend weak streams from the reverberatory furnace with stronger streams from other smelting equipment (Section 3). An analysis of a typical smelter system that could be built using multihearth roasters (MHR) or a fluid-bed roaster (FBR), a reverberatory furnace (RF), and converters follows to demonstrate the potential of using blending in conjunction with processing modifications (e.g. oxygen enrichment) and flue gas desulfurization systems (FGD) for upgrading weak SO_2 streams. The final step passes the upgraded, blended gases to a sulfuric acid plant.

For this study a new smelting unit consisting of roasters, reverberatory furnaces, and converters is considered. Some of the techniques discussed in Section 3 are assumed to be inherent in design and operation of the new smelter. Practical leakage point elimination, pressure control, continuous charging, converter scheduling and advance converter off-gas collection systems are among the techniques used. Additionally, converter slag is not returned to the reverberatory furnace (Appendix D).

The primary copper smelter under consideration is a new unit constructed in the Southwestern United States. The facility consists of five MHR or one FBR, one RF, and three operating converters with one additional standby. A total of 1,400 ton/day concentrate will be processed which consists of 28 percent Cu, 30 percent S, 28 percent Fe, 6 percent Si, 3 percent Al_2O_3, and 5 percent others. This unit is considered typical of current smelters found in the Southwestern United States.

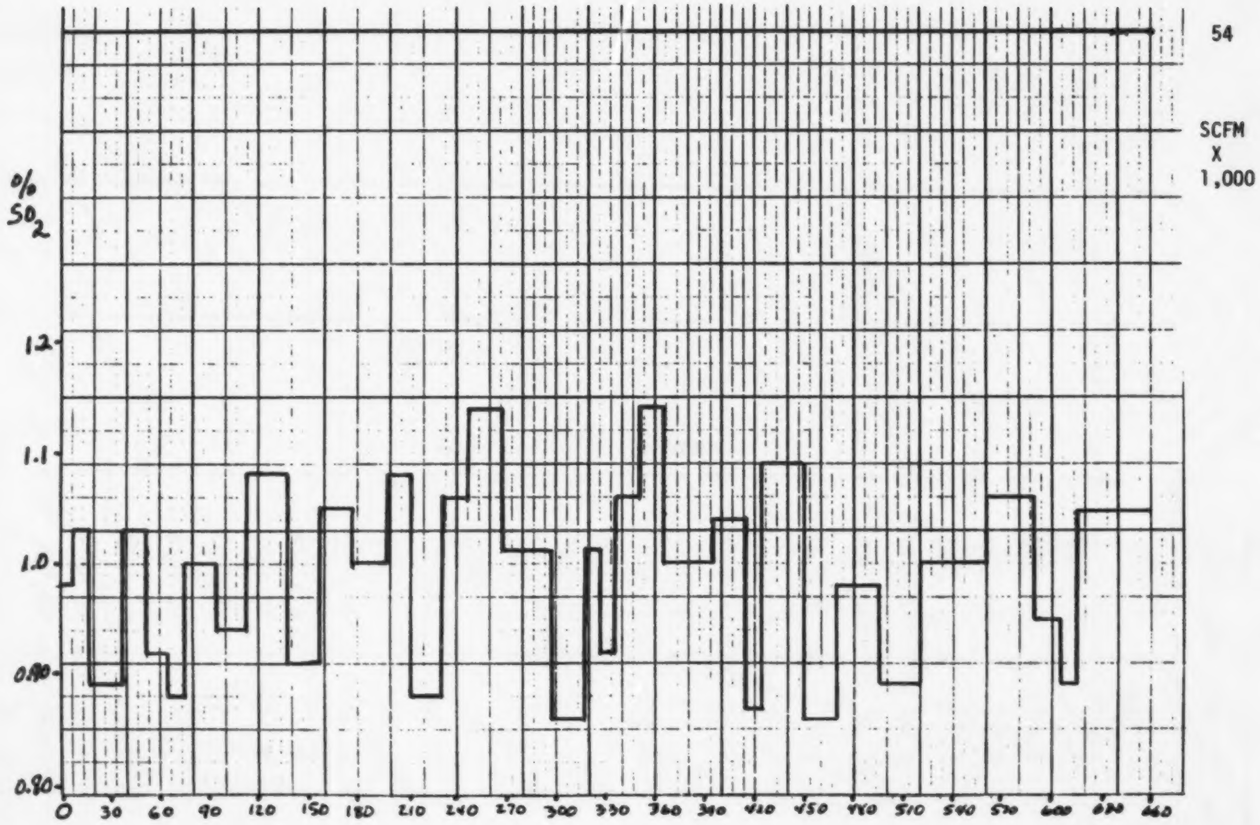
Typical Herreshoff or Wedge multihearth roasters processing 300 ton/day are used. Sulfur removal is approximately 32.9 percent.[133] Twenty to 50 percent SO_2 removal in MHR has been reported using domestic smelting technology based on information from seven smelters.[134] Additionally, volume and SO_2 concentrations of the roaster offgas are assumed to be fairly constant as indicated in the literature.[135] Thus, a 5 percent SO_2 at 42,000 scfm offgas is assumed and is in agreement with a sulfur balance and literature reports.[136,137,138] This SO_2 offgas strength may be high in comparison with existing units at some U.S. smelters because the latter are old and contain many leakage points allowing dilution air input. Theoretical calculations have indicated values up to 7 percent to be feasible (Appendix A).[139]

Assuming FBR can be used instead of MHR for processing dirty feed (Section 3), constant offgas characteristics are also assumed. The values to be used are 9.1 percent SO_2 at 23,600 scfm based on actual reported data.[37]

Reverberatory furnaces are typically the same throughout the copper industry with the major operating difference occurring between green and calcine charge processing. For this study, about 35 ton/day sulfur (8.25 percent) will be removed in the calcine charge reverberatory furnace. Again, the offgas volume will be considered constant at about 54,000 scfm. Although this value may be low for reverberatory furnace offgases in the U.S., it is consistent with new units in Japan and corresponds well with Inco data for a copper smelting handling similar feeds. The reverberatory SO_2 offgas concentration fluctuates due to calcine charging. The actual deviations from an average SO_2 concentration of 1 percent by volume (for calcine charge) were scaled down and proportioned from data on SO_2 versus time for Onahama Smelter (for green charge) in Japan (Appendix Y). Figure 6-1 shows gas characteristics assumed for the reverberatory furnace which are summarized in Table 6-1. It should be noted that a continuous side charging technique for calcine charge can minimize these fluctuations as noted in Appendix C.

The converters will treat matte of 24.5 percent S, 40 percent Cu, 26 percent Fe, and some Fe_3O_4. A sulfur balance indicates 237 ton/day sulfur (56.43 percent) will be removed during the various slag and copper blows.[140] Due to the batch-type operation of a converter cycle, there are fluctuations in both SO_2 and volumes of the offgas which can be seen in Figure 6-2 and are summarized in Table 6-2. The average values assumed are 4.5 percent SO_2 at 82,000 scfm. These values were based on the initial sulfur balance, and reported volumes of offgas of 32,000 to 45,000 scfm per converter.[141] In addition, converter programming was also assumed (Appendix H) with the basic criteria of copper blows on only one converter at a time.

Additional assumed cases for the blending scenarios include oxygen enrichment of the reverberatory air, the use of a lime or limestone system for reverberatory offgas neutralization, and the use of an MgO or citrate enrichment system for upgrading SO_2 in the offgases.



TIME MINUTES

Figure 6-1. Reverberatory Furnace Offgas Characteristics

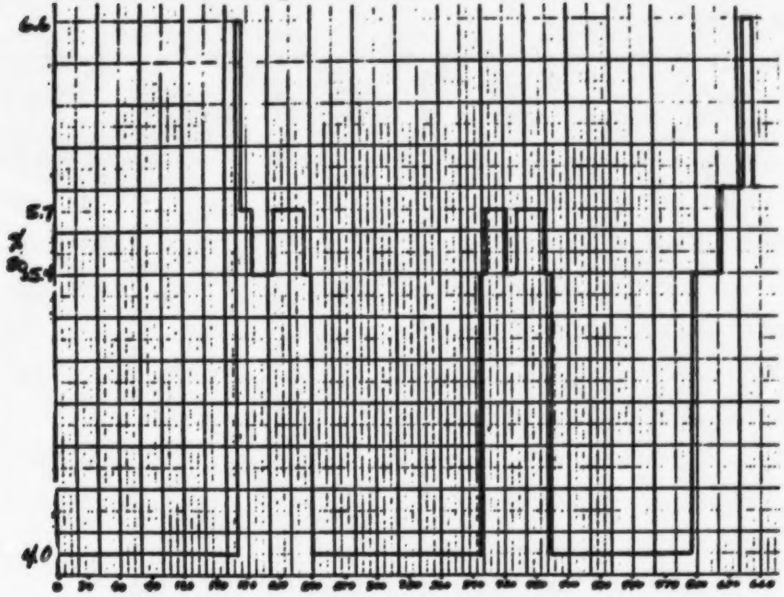
Table 6-1. REVERBERATORY OFFGAS VOLUME AND SO_2 PROFILES

No Oxygen Enrichment					
Time (min)	SO_2(%)	Volume (scfm)	Time (min)	SO_2(%)	Volume (scfm)
7.5	0.98	54,000	20	0.86	54,000
10	1.03	54,000	25	0.98	54,000
20	0.89	54,000	25	0.89	54,000
15	1.03	54,000	40	1.0	54,000
12.5	0.92	54,000	30	1.06	54,000
10	0.88	54,000	15	0.95	54,000
20	1.0	54,000	10	0.89	54,000
17.5	0.94	54,000	45	1.05	54,000
25	1.08	54,000			
20	0.91	54,000			
20	1.05	54,000			
20	1.0	54,000			
15	1.08	54,000			
20	0.88	54,000			
15	1.06	54,000			
20	1.14	54,000			
30	1.01	54,000			
20	0.86	54,000			
10	1.01	54,000			
7.5	0.92	54,000			
15	1.06	54,000			
15	1.14	54,000			
30	1.0	54,000			
20	1.04	54,000			
10	0.97	54,000			
25	1.09	54,000			

Table 6-1. REVERBERATORY OFFGAS VOLUME AND SO_2 PROFILES (CONCLUDED)

With O_2 Enrichment					
Time (min)	SO_2(%)	Volume (scfm)	Time (min)	SO_2(%)	Volume (scfm)
7.5	1.37	41,800	20	1.20	41,800
10	1.44	41,800	25	1.37	41,800
20	1.25	41,800	25	1.25	41,800
15	1.44	41,800	40	1.4	41,800
12.5	1.29	41,800	30	1.48	41,800
10	1.23	41,800	15	1.33	41,800
20	1.40	41,800	10	1.25	41,800
17.5	1.32	41,800	45	1.47	41,800
25	1.51	41,800			
20	1.27	41,800			
20	1.47	41,800			
20	1.40	41,800			
15	1.51	41,800			
20	1.23	41,800			
15	1.48	41,800			
20	1.60	41,800			
30	2.41	41,800			
20	1.20	41,800			
10	1.41	41,800			
7.5	1.29	41,800			
15	1.48	41,800			
15	1.60	41,800			
30	1.40	41,800			
20	1.46	41,800			
10	1.36	41,800			
25	1.53	41,800			

CONVERTER SO_2 OFFGAS VERSUS TIME



CONVERTER OFFGAS VOLUME VERSUS TIME

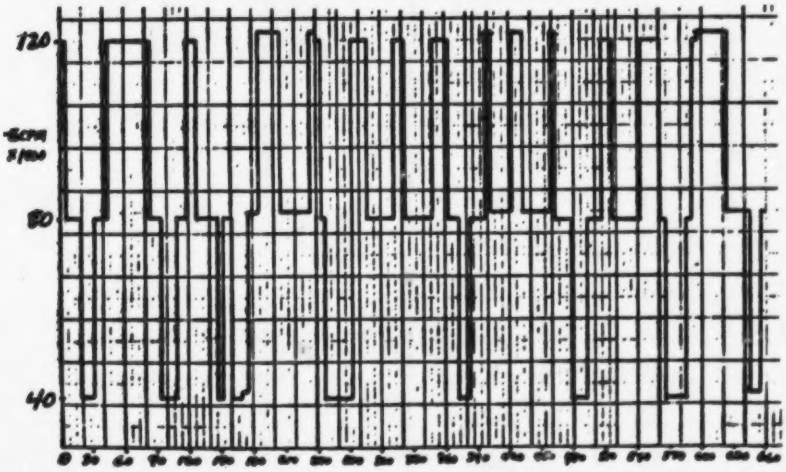


Figure 6-2. Converter Offgas Characteristics

Table 6-2. CONVERTER OFFGAS VOLUME AND SO_2 PROFILES

O_2 and No O_2 Enrichment					
Time (min)	SO_2(%)	Volume (scfm)	Time (min)	SO_2(%)	Volume (scfm)
5	4.0	120,000	10	5.4	122,000
15	4.0	80,000	25	5.7	82,000
11	4.0	40,000	5	5.4	122,000
14	4.0	80,000	16	4.0	80,000
40	4.0	120,000	14	4.0	40,000
10	4.0	80,000	15	4.0	80,000
15	4.0	40,000	9	4.0	120,000
9	4.0	80,000	26	4.0	80,000
10	4.0	120,000	19	4.0	120,000
20	4.0	80,000	5	4.0	80,000
5	4.0	40,000	19	4.0	40,000
7	4.0	80,000	5	4.0	80,000
10	4.0	40,000	5	4.0	120,000
5	6.6	42,000	29	5.4	122,000
10	5.7	82,000	20	5.7	82,000
20	5.4	122,000	10	6.6	42,000
29	5.7	82,000	5	5.7	82,000
5	5.4	122,000			
5	4.0	120,000			
4	4.0	80,000			
24	4.0	40,000			
15	4.0	120,000			
25	4.0	80,000			
10	4.0	120,000			
25	4.0	80,000			
15	4.0	120,000			
10	4.0	80,000			
11	4.0	40,000			
14	4.0	80,000			
5	5.4	122,000			
20	5.7	82,000			

Oxygen enrichment as used in this study for a calcine-charged reverberatory furnace results in producing a total air oxygen content of about 26 percent. This amount enriches the average SO_2 in the offgas to 1.4 percent by volume, while decreasing the volume flow to 41,800 scfm. These values are based on actual data from a calcine charged reverberatory furnace.[142] Although these amounts are low when compared to oxygen enrichment of a green-charged reverberatory furnace, there is relatively little information as to the extent of oxygen enrichment for calcine-charged reverberatory furnaces. Oxygen enrichment up to 60 percent has resulted in SO_2 offgas strengths as high as 7.0 percent by volume for green charge reverberatory furnaces.[143] For the oxygen enrichment case, the multihearth roaster offgas was taken as 5 percent SO_2 at 42,096 scfm and the fluid-bed roaster offgas as 9.1 percent SO_2 at 23,100 scfm to maintain a sulfur balance.

The MgO and citrate systems reportedly maintain SO_2 offgas concentrations of 10 and 95 percent, respectively.[144,145] Using these numbers and making a sulfur balance assuming a 90 percent efficiency of the FGD system, values were obtained for offgas volume flow rates. Additionally, it is assumed that no oxygen will be released with the citrate offgases, while about 8 percent oxygen will be generated from the calciner of the MgO system - comparable to a MHR.

Oxygen concentrations for the various smelting equipment offgases are assumed to be constant. Values are based on average gas characteristics from the various smelting equipment. These values provide the basis for determining if the O_2 to SO_2 ratio is sufficient for sulfuric acid production or if dilution air is required to meet the acid plant needs in the conversion of SO_2 to SO_3.

Values based on the aforementioned assumptions are summarized in Table 6-3 and are used in determining the blended gas characteristics discussed in the following sections.

Table 6-3. BASIS: BLENDING SCHEMES

	No O_2 Enrichment	O_2 Enrichment
MHR	5.0% SO_2 at 43,000 SCFM	5.0% SO_2 at 42,096 SCFM
FBR	9.1% SO_2 at 23,600 SCFM	9.1% SO_2 at 23,100 SCFM
RF (Ave)	1.0% SO_2 at 54,000 SCFM	1.4% SO_2 at 41,800 SCFM
Conv (Ave)	4.5% SO_2 at 82,000 SCFM	4.5% SO_2 at 82,000 SCFM

MHR $SO_2 + O_2$ = 18%; FBR $SO_2 + O_2$ = 13.1%
RF $SO_2 + O_2$ = 4%
Converter $SO_2 + O_2$ = 14% (slag below)
$SO_2 + O_2$ = 20% (copper below)
MgO System $SO_2 + O_2$ = 18%
Citrate System SO_2 = 95%, H_2O = 5%

Volume and SO_2 constant off FGD systems (90 percent efficient)

	No O_2 Enrichment	O_2 Enrichment
MgO	10% SO_2 at 4,860 SCFM	10% SO_2 at 5,270 SCFM
Citrate	95% SO_2 at 510 SCFM	95% SO_2 at 550 SCFM

6.1.3 BLENDING SCENARIOS FOR REVERBERATORY FURNACE SO_2 CONTROL

Figures 6-3 through 6-9 show the various systems devised for handling the SO_2 offgases from the copper smelter under consideration. As shown, there are two basic cases to be analyzed (refer to Figure 6-3). One uses MHR, RF, and converters, while the other uses FBR, RF, and converters. To these basic cases, possible blending scenarios utilizing O_2 enrichment, FGD systems, and acid plants are examined for controlling RF SO_2 offgases.

Based on the aforementioned blending scenarios and the assumptions presented in Section 6.1.2, the various blended gas characteristics were calculated over 11 hours - one converter cycle (see Appendix Y). These calculations reveal that the O_2 to SO_2 ratios are sufficient to preclude any dilution air addition at the acid plants. Also, the SO_2 concentrations are high enough (greater than 4.5 percent) in all but four cases (1) MHR + Conv. + RF (2) same except RF O_2 enrichment (3) FBR + Conv. + RF and (4) same except RF O_2 enrichment to allow processing in a double contact sulfuric acid plant. The volume and SO_2 concentrations fluctuate mainly because of the fluctuating converter offgas influence.

Table 6-4 lists the general characteristics to be considered in designing systems for treating RF offgases in FGD systems prior to blending. The blending scenarios as presented include design characteristics for FGD systems and acid plants - maximum volumes and average SO_2 concentrations. Minimum and average gas characteristics are included to aid the designer in determining if any additional process equipment will be needed to accommodate large fluctuations.

Scenarios Nos. 17 and 18 in Table 6-4 are for new smelters operating under the existing NSPS excluding RF offgases from any control and serve as a model case for comparing those blending scenarios which have RF offgas control. They assume that "dirty

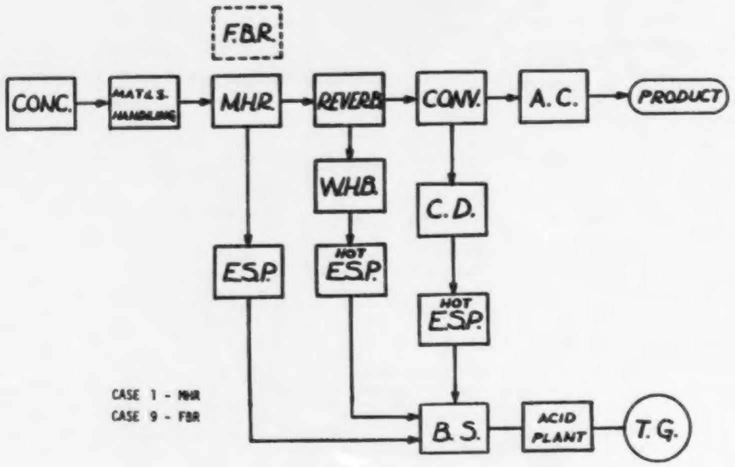

F.B.R.
CONC.
MAT'L & SI. HANDLING
MHR
REVERB
CONV.
A.C.
PRODUCT
W.H.B.
C.D.
E.S.P.
HOT E.S.P.
HOT E.S.P.
CASE 1 - MHR
CASE 9 - FBR
B.S.
ACID PLANT
T.G.

Figure 6-3. Flowsheet for Blending Copper Smelter Offgases

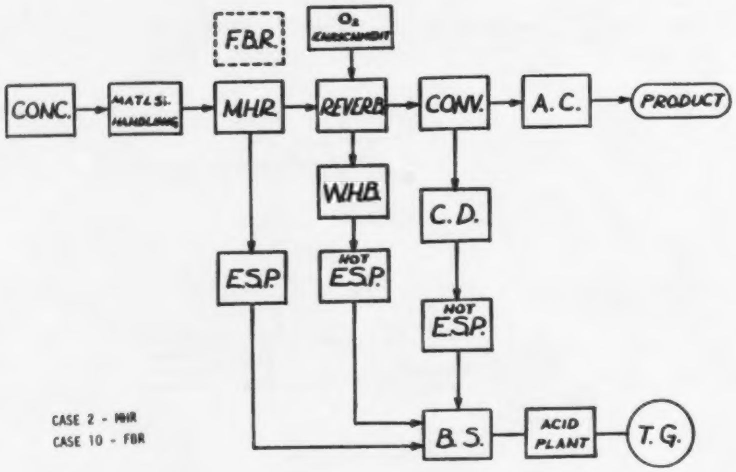

F.B.R.
O_2 ENRICHMENT
CONC.
MAT'L & SI. HANDLING
MHR
REVERB
CONV.
A.C.
PRODUCT
W.H.B.
C.D.
E.S.P.
HOT E.S.P.
HOT E.S.P.
CASE 2 - MHR
CASE 10 - FBR
B.S.
ACID PLANT
T.G.

Figure 6-4. Flowsheet for Blending Copper Smelter Offgases Using Oxygen Enrichment

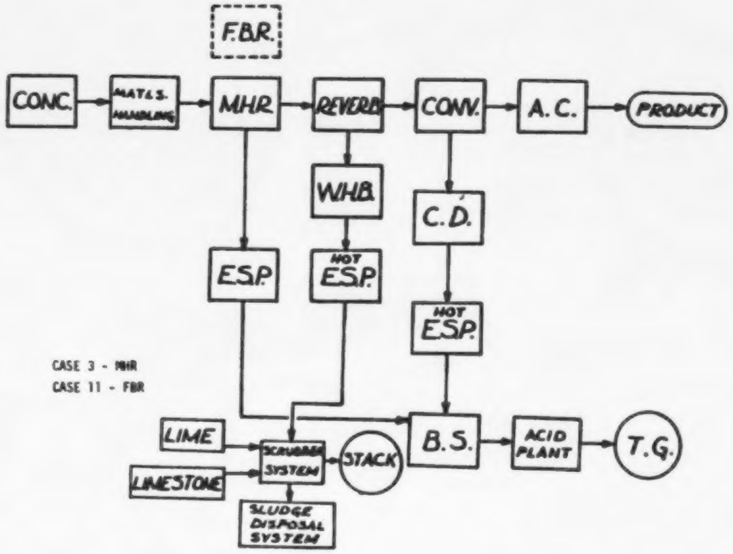

F.B.R.
CONC.
MAT'LS. HANDLING
MHR
REVERB
CONV.
A. C.
PRODUCT
W.H.B.
C.D.
E.S.P.
HOT E.S.P.
HOT E.S.P.
CASE 3 - MHR
CASE 11 - FBR
LIME
LIMESTONE
SCRUBBER SYSTEM
STACK
SLUDGE DISPOSAL SYSTEM
B.S.
ACID PLANT
T.G.

Figure 6-5. Flowsheet for Blending Copper Smelter Offgases Using Nonregenerative FGD Systems

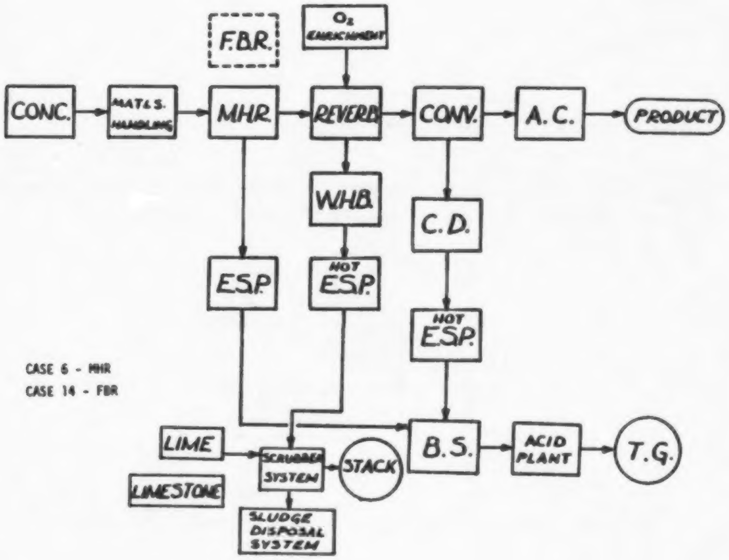

F.B.R.
O2 ENRICHMENT
CONC.
MAT'LS. HANDLING
MHR
REVERB
CONV.
A. C.
PRODUCT
W.H.B.
C.D.
E.S.P.
HOT E.S.P.
HOT E.S.P.
CASE 6 - MHR
CASE 14 - FBR
LIME
LIMESTONE
SCRUBBER SYSTEM
STACK
SLUDGE DISPOSAL SYSTEM
B.S.
ACID PLANT
T.G.

Figure G-6. Flowsheet for Blending Copper Smelter Offgases Using Oxygen Enrichment and Nonregenerative FGD Systems

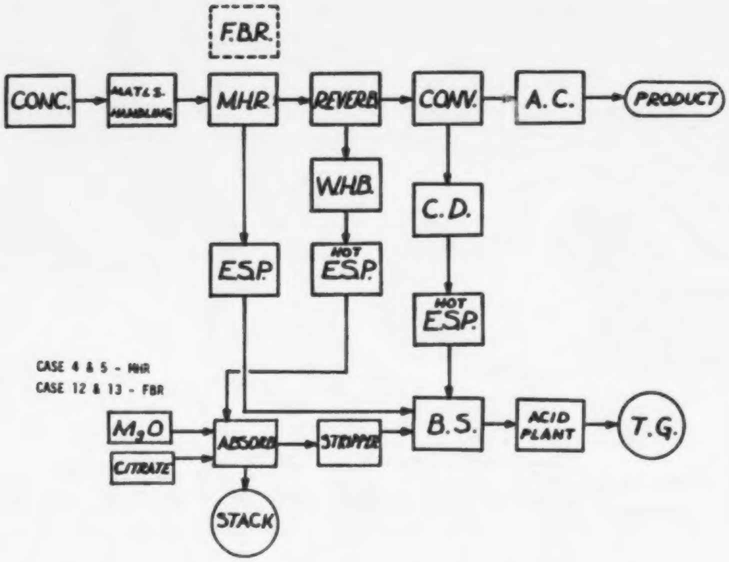

F.B.R.
CONC.
MAT'LS. HANDLING
MHR
REVERB
CONV.
A. C.
PRODUCT
W.H.B.
C. D.
E.S.P.
HOT E.S.P.
HOT E.S.P.
CASE 4 & 5 - MHR
CASE 12 & 13 - FBR
M_2O
CITRATE
ABSORB.
STRIPPER
B. S.
ACID PLANT
T. G.
STACK

Figure 6-7. Flowsheet for Blending Schemes Using Regenerative FGD Systems

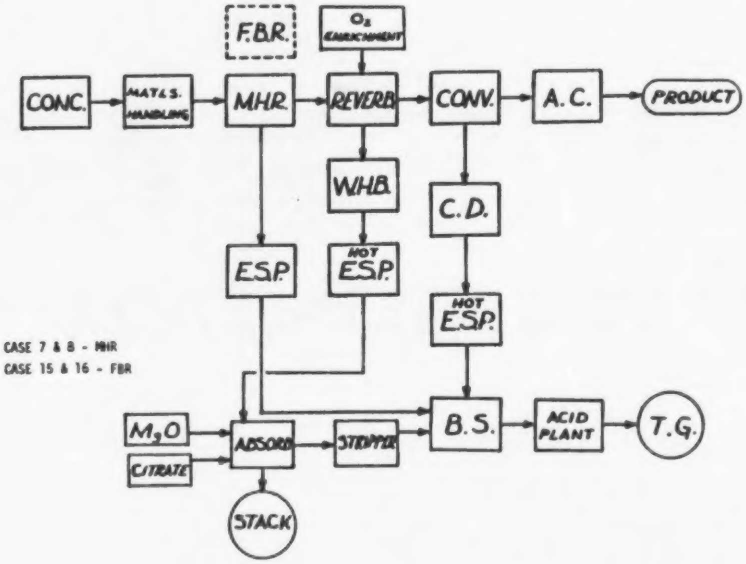

F.B.R.
O_2 ENRICHMENT
CONC.
MAT'LS. HANDLING
MHR
REVERB
CONV.
A. C.
PRODUCT
W.H.B.
C. D.
E.S.P.
HOT E.S.P.
HOT E.S.P.
CASE 7 & 8 - MHR
CASE 15 & 16 - FBR
M_2O
CITRATE
ABSORB.
STRIPPER
B. S.
ACID PLANT
T. G.
STACK

Figure 6-8. Flowsheet for Blending Copper Smelter Offgases Using Oxygen Enrichment and Regenerative FGD Systems

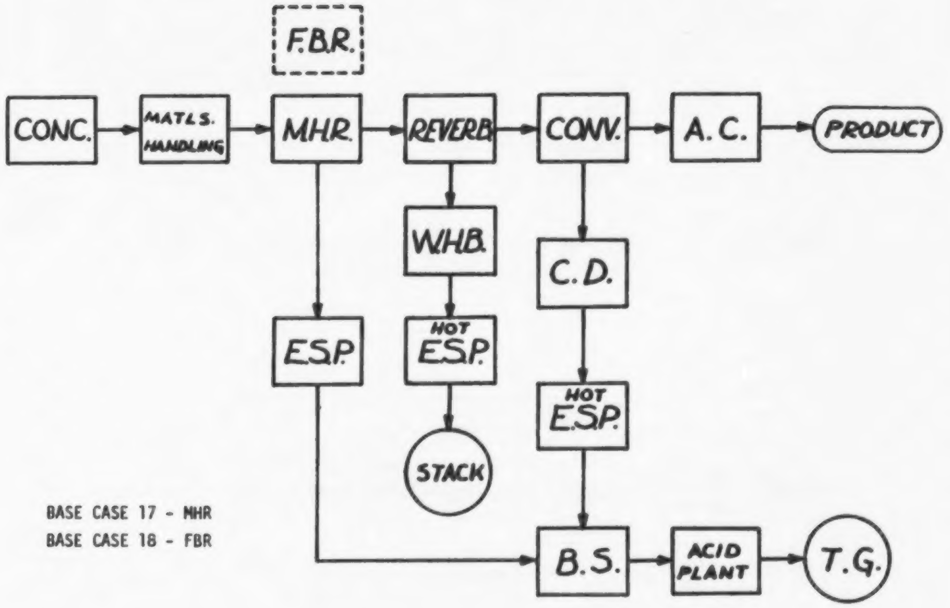

F.B.R.
CONC.
MATLS. HANDLING
M.H.R.
REVERB.
CONV.
A. C.
PRODUCT
W.H.B.
C. D.
E.S.P.
HOT E.S.P.
HOT E.S.P.
STACK
BASE CASE 17 - MHR
BASE CASE 18 - FBR
B. S.
ACID PLANT
T. G.

Figure 6-9. Flowsheet for Handling Copper Smelter SO_2 Offgases Dictated by the New Source Perforformance Standards

Table 6-4. BLENDING SCENARIOS FOR CONTROLLING SO_2 EMISSIONS FROM A NEW COPPER SMELTER PROCESSING 1,400 TPD-CONCENTRATE REVERBERATORY FURNACE GASES (ONLY) TO FGD SYSTEMS

Blending[a] Conditions	Volume to Acid Plant		Percent SO_2 to Acid Plant		Gas Characteristic to FGD System				SO_2 Emissions From Acid Plant (Max. TPD-SO_2)	Emissions From FGD System 90% Eff. (TPD-SO_2)	Uncontrolled SO_2 Emissions Including Fugitive (TPD-SO_2)	Total SO_2 Emissions to Atmosphere (Max. TPD-SO_2)	Percent Control Based on 840 TPD-SO_2 Input
	Maximum (Minimum) S C F M	Average (SCFM)	Max-imum (Min)	Ave-rage	Maximum (Minimum) S C F M	Maximum (Minimum) % SO_2	Average S C F M	Average % SO_2					
1. MHR + Conv. + RF[b] (SC/SA Acid Plant)	219,000 (137,000)	179,000	4.26 (3.09)	3.56					73.1	-	19.7	92.8	89
2. MHR + Conv. + RF (O_2 Enrich)[b] [SC/SA Acid Plant]	205,896 (123,896)	165,896	4.53 (3.41)	3.85					68.4	-	19.7	88.1	89.5
3. MHR + Conv.+(RF to Lime/Limestone)	165,000 (83,000)	125,000	5.30 (4.52)	4.67	54,000 (54,000)	1.14 (.86)	54,000	1.0	13.8	6.9	19.7	40.4	95.2
4. MHR + Conv. + (RF → MgO System)	169,860 (87,860)	129,860	5.43 (4.82)	4.87	54,000 (54,000)	1.14 (.86)	54,000	1.0	14.2	6.9	19.7	40.8	95.2
5. MHR + Conv. + (RF → Citrate)	165,510 (83,510)	125,510	5.58 (5.07)	5.04	54,000 (54,000)	1.14 (.86)	54,000	1.0	13.9	6.9	19.7	40.5	95.2
6. MHR + Conv.; RF (O_2 Enrich) → Lime/ Limestone	164,096 (82,096)	124,096	5.30 (4.51)	4.67	41,800 (41,800)	1.6 (1.2)	41,800	1.4	13.7	7.5	19.7	40.9	95.1
7. MHR + Conv.+ [RF (O_2 Enrich) → MgO]	169,366 (87,366)	129,366	5.45 (4.84)	4.89	41,800 (41,800)	1.6 (1.2)	41,800	1.4	14.1	7.5	19.7	41.3	95.1
8. MHR + Conv. + [RF O_2 Enrich) → Citrate]	164,646 (82,646)	124,646	5.60 (5.11)	5.07	41,800 (41,800)	1.6 (1.2)	41,800	1.4	13.8	7.5	19.7	41.0	95.1
9. FBR + RF + Conv.[b] (SC/SA Acid Plant)	199,600 (117,600)	159,600	4.67 (3.60)	3.66					66.7	-	20	86.7	89.7
10. FBR + Conv. + RF (O_2 Enrich)[b] [SC/SA Acid Plant]	186,900 (104,900)	146,900	4.99 (4.03)	4.34					62.5	-	20	82.5	90.2
11. FBR + Conv.; RF → Lime/Limestone	145,600 (63,600)	105,600	6.00 (5.89)	5.53	54,000 (54,000)	1.14 (.86)	54,000	1.0	12.2	6.9	20	39.1	95.3
12. FBR + Conv. + (RF → MgO System)	150,460 (68,460)	110,460	6.13 (6.18)	5.72	54,000 (54,000)	1.14 (.86)	54,000	1.0	12.5	6.9	20	39.4	95.3

Table 6-4. BLENDING SCENARIOS FOR CONTROLLING SO_2 EMISSIONS FROM A NEW COPPER SMELTER PROCESSING 1,400 TPD-CONCENTRATE REVERBERATORY FURNACE GASES (ONLY) TO FGD SYSTEMS (CONCLUDED)

Blending[a] Conditions	Volume to Acid Plant		Percent SO_2 to Acid Plant		Gas Characteristic to FGD System				SO_2 Emissions From Acid Plant (Max. TPD-SO_2)	Emissions From FGD System 90% Eff. (TPD-SO_2)	Uncontrolled SO_2 Emissions Including Fugitive (TPD-SO_2)	Total SO_2 Emissions to Atmosphere (Max. TPD-SO_2)	Percent Control Based on 840 TPD-SO_2 Input
					Maximum (Minimum)		Average						
	Maximum (Minimum) S C F M	Average (SCFM)	Max-imum (Min)	Ave-rage	S C F M	% SO_2	S C F M	% SO_2					
13. FBR + Conv. +(RF ➞ Citrate)	146,110 (64,110)	106,110	6.31 (6.60)	5.96	54,000 (54,000)	1.14 (.86)	54,000	1.0	12.2	6.9	20	39.1	95.3
14. FBR + Conv.; RF (O_2 Enrich) ➞ Lime/ Limestone	145,100 (63,100)	105,100	5.99 (5.87)	5.51	41,800 (41,800)	1.6 (1.2)	41,800	1.4	12.1	7.5	20	39.6	95.3
15. FBR + Conv. +[RF (O_2 Enrich) ➞ MgO]	150,370 (68,370)	110,370	6.13 (6.19)	5.73	41,800 (41,800)	1.6 (1.2)	41,800	1.4	12.5	7.5	20	40.0	95.2
16. FBR + Conv. +[RF (O_2 Enrich) ➞ Citrate]	145,650 (63,650)	105,650	6.33 (6.64)	5.98	41,800 (41,800)	1.6 (1.2)	41,800	1.4	12.2	7.5	20	39.7	95.3
17. MHR + Conv.; RF Un-controlled (Existing Standards)	165,000 (83,000)	125,000	5.30 (4.52)	4.67	-	-	-	-	13.8	-	89.1	102.9	87.2
18. FBR + Conv.; RF Un-controlled (Existing Standards)	145,600 (63,600)	105,600	6.0 (5.89)	5.53	-	-	-	-	12.2	-	89.4	101.6	87.9

[a] All blended offgases, unless otherwise indicated, are processed in a double contact sulfuric acid plant.

[b] Blended offgases processed in a single contact sulfuric acid plant.

feeds" can be processed in MHR as well as FBR because the latter are currently being used for some impurity combinations, Reference 146.

The maximum scfm to the acid plant, i.e., design criteria, for the various scenarios indicate that the acid plant design capacities will be similar for RF control via FGD systems and the model case. For scenarios Nos. 1, 2, 9, and 10, the acid plant design capacities are increased by the volume of gas off the RF; however, for these cases, single contact acid plants are required due to the SO_2 concentration - below 4.5 percent.

Gas characteristics to the FGD systems vary according to the use or nonuse of oxygen enrichment in the RF. The volumes to be handled by the FGD systems are 54,000 and 41,800 scfm for no oxygen enrichment and oxygen enrichment, respectively.

In addition, Table 6-4 lists the SO_2 control capabilities of the various scenarios. For those cases using FGD systems on RF offgases prior to blending, the control efficiencies are approximately 95 percent. Comparing this with the control realized under the NSPS, there is about an additional 7 percent SO_2 capture. For the cases where the RF offgases are merely blended and then sent to a single contact sulfuric acid plant, only a slight increase in SO_2 control is realized.

The major factor influencing total SO_2 control efficiency is whether the blended gases are processed in a double contact or single contact sulfur acid plant. As noted in Section 4, double contact acid plants release about 650 ppm SO_2, and single contact acid plants release about 2,600 ppm to the atmosphere. This indicates that single contact acid plants release about four times more SO_2 emissions as double contact acid plants.

Assumptions for Table 6-4 are summarized in Appendix Y.

In addition to calcine charge reverberatory furnace SO_2 control, the blending potential for green charged reverberatory furnaces should be addressed briefly. Although it is unlikely that future green charge reverberatory smelting facilities will be constructed in the future due to feed considerations, several existing facilities employ such smelting practices and as such any blending potential deserves discussion.

For the above case, one reverberatory furnace and four converters (three operating and one on standby) are considered to represent the new smelting facility. Offgas characteristics from the reverberatory furnace are assumed to be identical to those at the Onahama smelter in Japan - 55,000 scfm with 2.5 percent SO_2. The converter offgas characteristics are the same as for the calcine charge reverberatory furnace situation.

Table 6-5 lists the general characteristics to be considered in designing systems for total SO_2 control. Case A represents blending reverb and converter offgases and direct processing in an acid plant. For this case, the blended offgases are too low in SO_2 for direct processing in a double contact sulfuric acid plant and, as such, would require processing in a single contact acid plant.

Case B neutralizes reverb gases with a lime/limestone system and treats converter gases in an acid plant. Cases C and D use either the MgO or Citrate regenerative systems to concentrate the reverb gases, then blend with the converter gases and treat this blend in a sulfuric acid plant. These cases reduce the offgas volume to the acid plant but would require additional expenditures for the FGD system. For a comprehensive assessment of any blending feasibility, an economic evaluation is required. The reduction in acid plant handling capacity could offset the costs associated with the FGD system and provide economic incentives. This aspect requires further evaluation for economic implications.

Table 6-5. BLENDING SCENARIOS FOR CONTROLLING SO_2 EMISSIONS FROM A NEW GREEN CHARGE COPPER SMELTING FACILITY

Blending Conditions[a]	Volume to Acid Plant		Percent SO_2 to Acid Plant		Gas Characteristic to FGD System				SO_2 Emissions From Acid Plant (Max. TPD-SO_2)	Emissions From FGD System 90% Eff. (TPD-SO_2)	Uncontrolled SO_2 Emissions Including Fugitive (TPD-SO_2)	Total SO_2 Emissions to Atmosphere (Max. TPD-SO_2)	Percent Control Based on 840 TPD-SO_2 Input
	Maximum (Minimum) SCFM	Average SCFM	Maximum (Min)	Average	Maximum (Minimum)		Average						
					SCFM	% SO_2	SCFM	% SO_2					
A. RF + Conv SC/SA Acid Plant[b]	177,000	137,000	4.6 (2.9)	3.7	----	---	----	---	25.3	---	20	45.3	94.6
B. [RF (Lime/Limestone)]: Conv	122,000 (40,000)	82,000	5.4 (4.0)	4.5	55,000 (55,000)	2.85 (2.15)	55,000	2.5	2.8	17.7	20	40.5	95.2
C. [RF MgO] + Conv	136,110 (50,640)	94,380	5.88 (5.26)	5.22	55,000 (55,000)	2.85 (2.15)	55,000	2.5	3.65	17.7	20	41.4	95.1
D. (RF Citrate) + Conv	123,490 (41,120)	83,300	6.48 (6.48)	5.92	55,000 (55,000)	2.85 (2.15)	55,000	2.5	3.76	17.7	20	41.5	95.1

[a] All blended offgases, unless otherwise indicated, are processed in a double contact sulfuric acid plant.

[b] Blended offgases processed in a single contact sulfuric acid plant.

6.1.4 OTHER BLENDING CONSIDERATIONS

This section will examine blending scenarios which will enrich the SO_2 concentrations of the gases sent to the acid plant as well as decrease the volumes to be handled by such systems. The strategy used will entail processing different combinations of smelting equipment offgases, other than only the RF, in FGD systems prior to blending in hopes of finding an economic optimization. The FGD systems applicable to such an approach include only the MgO and citrate since these systems not only reduce the offgases but also concentrate the resulting offgas SO_2. Figures 6-10 through 6-19 show these various systems devised to handle offgases from the copper smelter assumed for this study.

The lime or limestone FGD systems are excluded since their application for processing stronger SO_2 concentrations may be limited both economically and physically (Section 5.2). The scenarios, as discussed herein, typically will process offgases from MHR, FBR, or converter gases along with or without those of the RF. Thus, these processed gases will have higher SO_2 concentrations due to the assumed SO_2 concentrations from these process equipments.

Table 6-6 is similar to Table 6-4 and considers the characteristics of the blended systems as indicated. All assumptions considered for Table 6-4 are applicable here (see Appendix Y).

Table 6-6 indicates that the design capacity for the acid plants (based on maximum volume flow) will change considerably from the base cases, depending on the scenario. Reductions in volume achieved are as much as 79 percent (i.e., case No. 50); however, the O_2/SO_2 ratios of the resulting blended gases may not be sufficient for conversion of SO_2 to SO_3 (refer to Section 4).

Table 6-7 lists the O_2/SO_2 ratios for those scenarios presented in Table 6-6. As shown, many of these ratios fall below the minimal 1.2 and, therefore, would require additional oxygen for proper conversion. Case Nos. 19, 23, 27, 30, 31, 32, 34, 35, 36, 38, 39, 40, 42, 43, 44, 46, 47, 48, 50, 51, 53, 55, 56, 57, and 58 are all

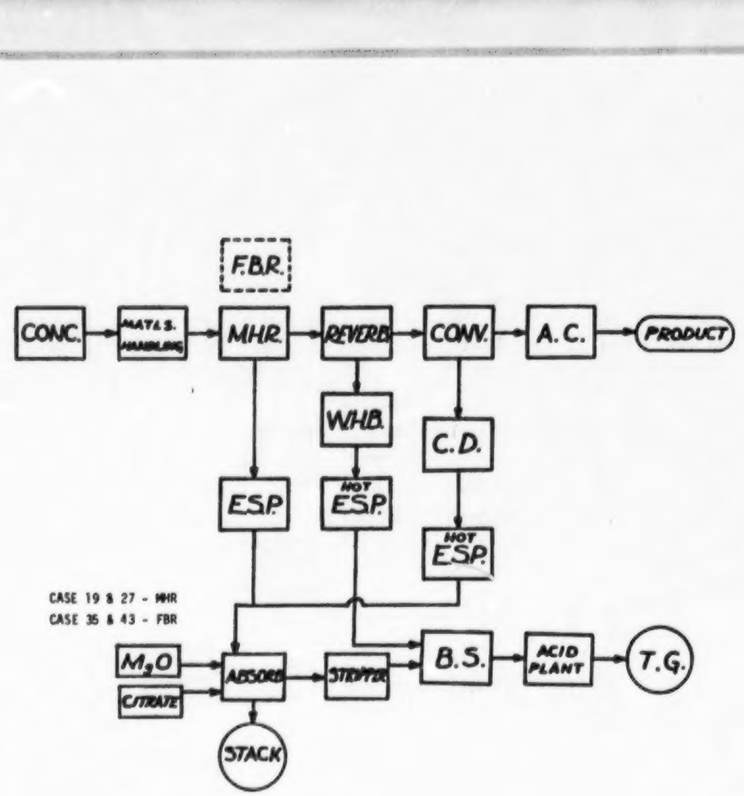

F.B.R.
CONC.
MAT'L S. HANDLING
MHR.
REVERB.
CONV.
A.C.
PRODUCT
W.H.B.
C.D.
E.S.P.
HOT E.S.P.
HOT E.S.P.
CASE 19 & 27 - MHR
CASE 35 & 43 - FBR
M₂O
CITRATE
ABSORB.
STRIPPER
B.S.
ACID PLANT
T.G.
STACK

Figure 6-10. Flowsheet for Blending Schemes Using Regenerative FGD Systems

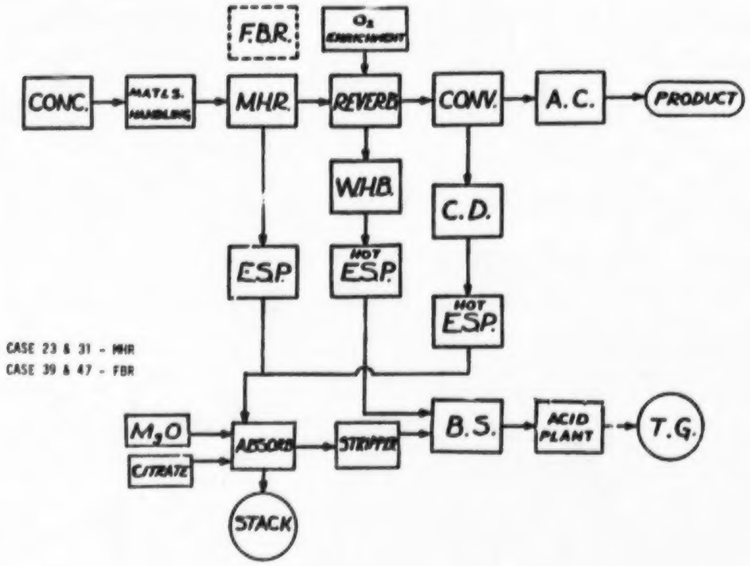

F.B.R.
O₂ ENRICHMENT
CONC.
MAT'L S. HANDLING
MHR.
REVERB.
CONV.
A.C.
PRODUCT
W.H.B.
C.D.
E.S.P.
HOT E.S.P.
HOT E.S.P.
CASE 23 & 31 - MHR
CASE 39 & 47 - FBR
M₂O
CITRATE
ABSORB.
STRIPPER
B.S.
ACID PLANT
T.G.
STACK

Figure 6-11. Flowsheet for Blending Copper Smelter Offgases Using Oxygen Enrichment and Regenerative FGD Systems

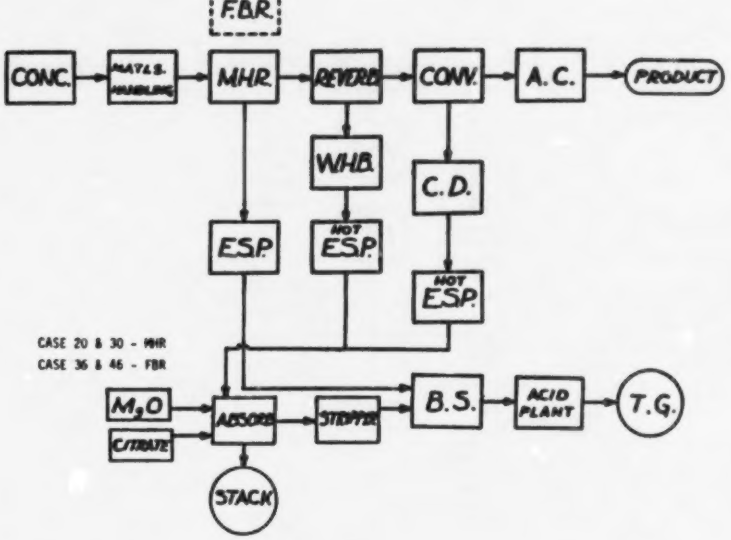

F.B.R.
CONC.
MAT'LS. HANDLING
MHR.
REVERB.
CONV.
A. C.
PRODUCT
W.H.B.
C. D.
E.S.P.
HOT E.S.P.
HOT E.S.P.
CASE 20 & 30 - MHR
CASE 36 & 46 - FBR
M_gO
CITRATE
ABSORB.
STRIPPER
B.S.
ACID PLANT
T.G.
STACK

Figure 6-12. Flowsheet for Blending Schemes Using Regenerative FGD Systems

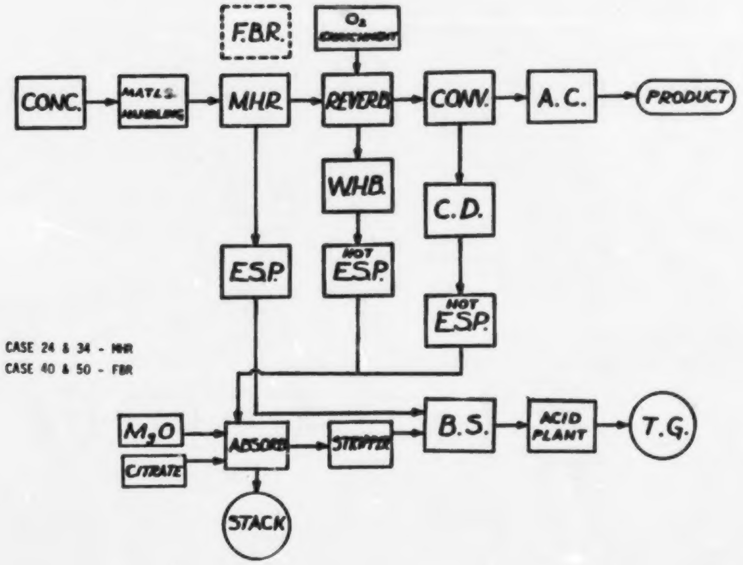

F.B.R.
O_2 ENRICHMENT
CONC.
MAT'LS. HANDLING
MHR.
REVERB.
CONV.
A. C.
PRODUCT
W.H.B.
C. D.
E.S.P.
HOT E.S.P.
HOT E.S.P.
CASE 24 & 34 - MHR
CASE 40 & 50 - FBR
M_gO
CITRATE
ABSORB.
STRIPPER
B.S.
ACID PLANT
T.G.
STACK

Figure 6-13. Flowsheet for Blending Copper Smelter Offgases Using Oxygen Enrichment and Regenerative FGD Systems

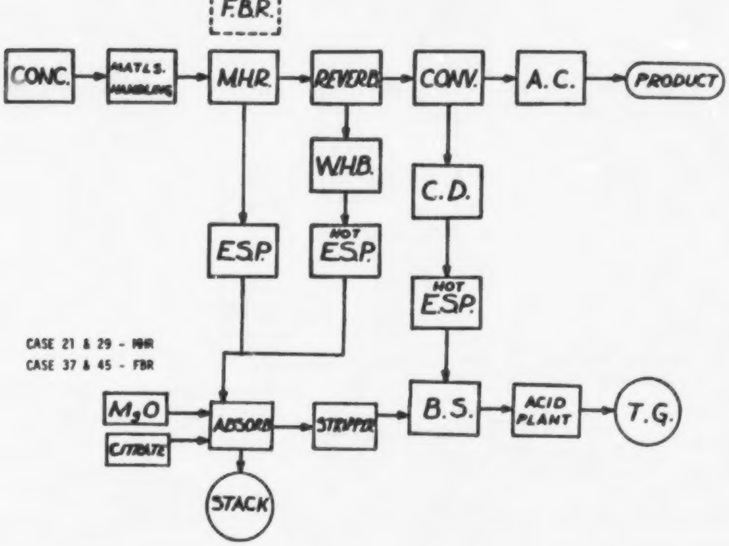

F.B.R.
CONC.
MAT'LS. HANDLING
MHR
REVERB.
CONV.
A.C.
PRODUCT
WHB
C.D.
ESP
HOT ESP
HOT ESP
CASE 21 & 29 - MHR
CASE 37 & 45 - FBR
M2O
CITRATE
ABSORB.
STRIPPER
B.S.
ACID PLANT
T.G.
STACK

Figure 6-14. Flowsheet for Blending Schemes Using Regenerative FGD Systems

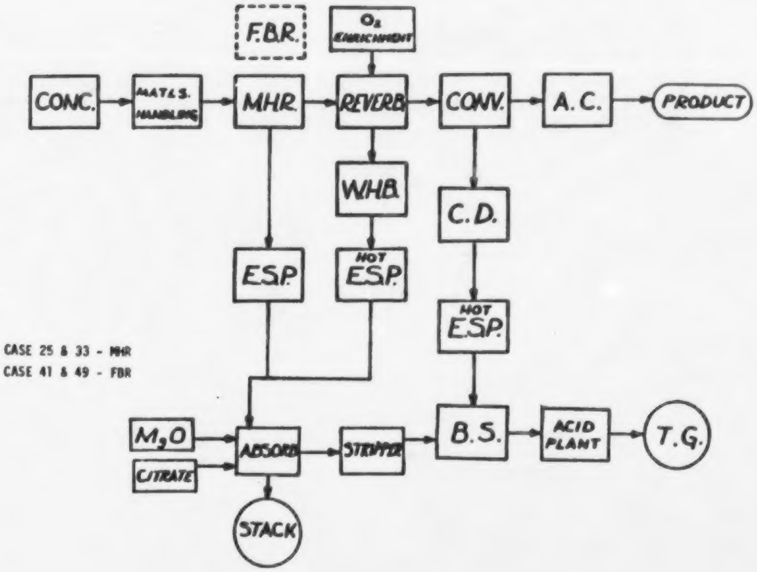

F.B.R.
O2 ENRICHMENT
CONC.
MAT'LS. HANDLING
MHR
REVERB.
CONV.
A.C.
PRODUCT
WHB
C.D.
ESP
HOT ESP
HOT ESP
CASE 25 & 33 - MHR
CASE 41 & 49 - FDR
M2O
CITRATE
ABSORB.
STRIPPER
B.S.
ACID PLANT
T.G.
STACK

Figure 6-15. Flowsheet for Blending Copper Smelter Offgases Using Oxygen Enrichment and Regenerative FGD Systems

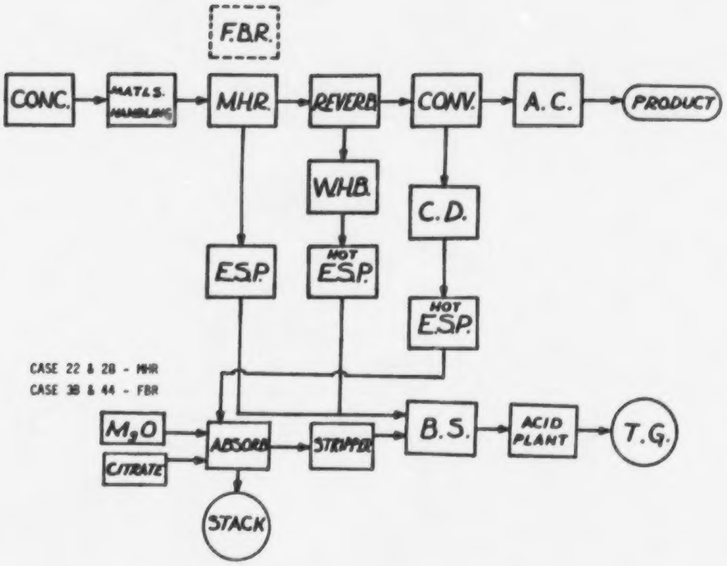

F.B.R.
CONC.
MAT'L S. HANDLING
M.H.R.
REVERB.
CONV.
A. C.
PRODUCT
W.H.B.
C. D.
E.S.P.
HOT E.S.P.
HOT E.S.P.
CASE 22 & 28 - MHR
CASE 38 & 44 - FBR
M$_2$O
CITRATE
ABSORB.
STRIPPER
B. S.
ACID PLANT
T. G.
STACK

Figure 6-16. Flowsheet for Blending Schemes Using Regenerative FGD Systems

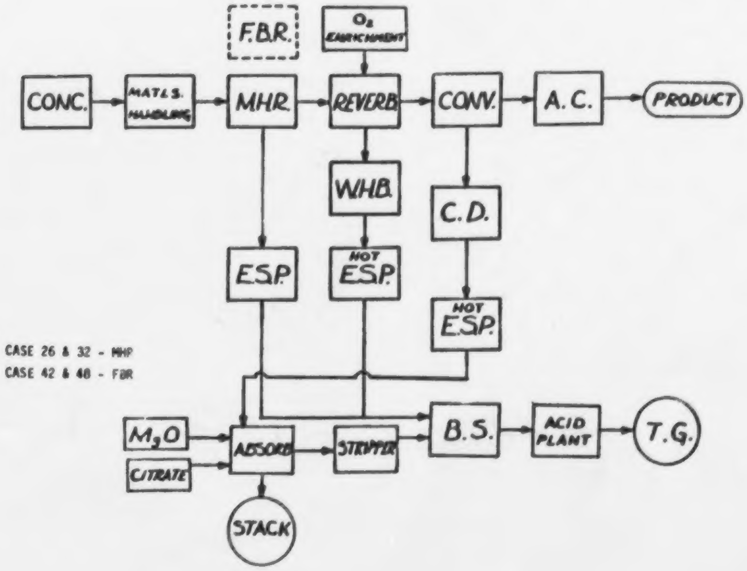

F.B.R.
O$_2$ ENRICHMENT
CONC.
MAT'L S. HANDLING
M.H.R.
REVERB.
CONV.
A. C.
PRODUCT
W.H.B.
C. D.
E.S.P.
HOT E.S.P.
HOT E.S.P.
CASE 26 & 32 - MHP
CASE 42 & 48 - FBR
M$_2$O
CITRATE
ABSORB.
STRIPPER
B. S.
ACID PLANT
T. G.
STACK

Figure 6-17. Flowsheet for Blending Copper Smelter Offgases Using Oxygen Enrichment and Regenerative FGD Systems

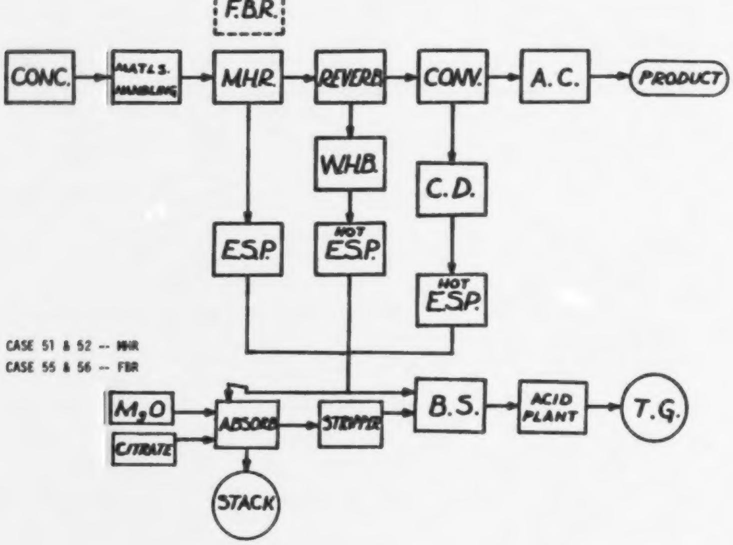

F.B.R.
CONC.
MAT'LS. HANDLING
MHR
REVERB
CONV.
A.C.
PRODUCT
W.H.B.
C.D.
E.S.P.
HOT E.S.P.
HOT E.S.P.
CASE 51 & 52 -- MHR
CASE 55 & 56 -- FBR
M2O
CITRATE
ABSORB
STRIPPER
B.S.
ACID PLANT
T.G.
STACK

Figure 6-18. Flowsheet for Blending Schemes Using Regenerative FGD Systems

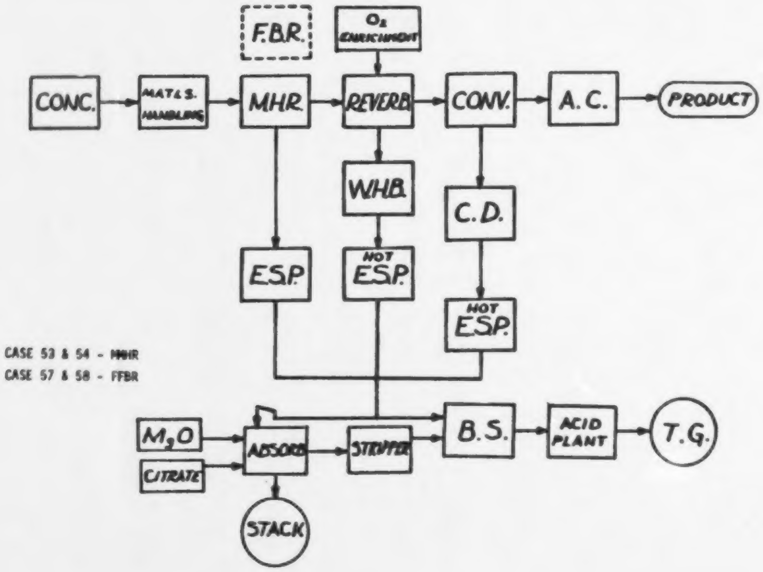

F.B.R.
O2 ENRICHMENT
CONC.
MAT'LS. HANDLING
MHR
REVERB
CONV.
A.C.
PRODUCT
W.H.B.
C.D.
E.S.P.
HOT E.S.P.
HOT E.S.P.
CASE 53 & 54 - MHR
CASE 57 & 58 - FFBR
M2O
CITRATE
ABSORB
STRIPPER
B.S.
ACID PLANT
T.G.
STACK

Figure 6-19. Flowsheet for Blending Copper Smelter Offgases Using Oxygen Enrichment and Regenerative FGD Systems

Table 6-6. ADDITIONAL BLENDING SCENARIOS FOR CONTROLLING SO_2 EMISSIONS FROM A NEW COPPER SMELTER PROCESSING 1,400 TPD-CONCENTRATE CONSIDERING COMBINATIONS OF ALL SMELTING EQUIPMENT OFFGASES

Blending[a] Conditions	Volume to Acid Plant		Percent SO_2 to Acid Plant		Gas Characteristic to FGD System				SO_2 Emissions From Acid Plant (Max. TPD-SO_2)	Emissions From FGD System 90% Eff. (TPD-SO_2)	Uncontrolled SO_2 Emissions Including Fugitive (TPD-SO_2)	Total SO_2 Emissions to Atmosphere (Max. TPD-SO_2)	Percent Control Based on 840 TPD-SO_2 Input
	Maximum (Minimum) S C F M	Average (SCFM)	Maximum (Min)	Average	Maximum (Minimum)		Average						
					S C F M	% SO_2	S C F M	% SO_2					
19. (Conv. → MgO System)+ (MHR → MgO System)+RF	132,642 (87,750)	106,560	6.39 (4.38)	5.44	165,000 (83,000)	4.67	125,000	5.3 4.52	11.1	75.1	19.7	105.9	87.4
20. (RF → MgO System) + (Conv. → MgO System) + MHR	107,832 (61,580)	81,070	8.01 (6.51)	7.35	176,000 (94,000)	4.09 (2.20)	136,000	3.11	9.0	54.4	19.7	83.1	90.1
21. (RF → MgO System)+(MHR → MgO Syst) + Conv.	146,890 (63,530)	106,210	6.18 (6.22)	5.75	97,000 (97,000)	2.85 (2.70)	97,000	2.77	12.3	34.5	19.7	66.5	92.1
22. (Conv. → MgO System)+ RF + MHR	156,292 (111,400)	130,210	5.56 (3.64)	4.62	122,000 (40,000)	5.4 (4.0)	82,000	4.5	13.0	47.4	19.7	80.1	90.5
23. (Conv. → MgO System)+ (MHR → MgO System)+ RF (O_2 Enrichment)	120,035 (75,143)	93,953	7.07 (5.10)	6.17	164,096 (82,096)	5.30 (4.51)	124,096	4.67	104.2	87.6	19.7	104.2	87.6
24. [RF (O_2 Enrichment) → MgO]+(Conv. → MgO System)+ MHR	107,407 (61,010)	80,573	8.04 (6.55)	7.39	163,800 (81,800)	4.43 (2.57)	123,800	3.45	8.9	54.9	19.7	83.5	90.1
25. [RF (O_2 Enrichment) → MgO]+(MHR → MgO System)+ Conv.	146,962 (63,458)	106,210	6.18 (6.22)	5.75	83,896 (83,896)	3.31 (3.11)	83,896	3.21	12.3	34.6	19.7	66.6	92.1
26. (Conv. → MgO System)+ MHR + RF (O_2 Enrich)	143,188 (98,296)	117,106	6.08 (4.12)	5.13	122,000 (40,000)	5.4 (4.0)	82,000	4.5	12.0	47.4	19.7	79.1	90.6
27. (Conv. → Citrate) + (MHR → Citrate)+ RF	62,278 (57,553)	59,533	13.62 (6.67)	9.74	165,000 (83,000)	5.3 (4.52)	125,000	4.67	5.2	75.1	19.7	100.0	88.1
28. (Conv. → Citrate) + MHR + RF	103,241 (98,516)	100,496	8.42 (4.12)	5.98	122,000 (40,000)	5.4 (4.0)	82,000	4.5	8.6	47.4	19.7	75.7	91.0
29. (RF → Citrate)+(MHR → Citrate)+ Conv.	122,586 (42,467)	84,548	7.40 (9.31)	7.23	97,000 (97,000)	2.85 (2.70)	97,000	2.77	10.3	34.5	19.7	64.5	92.3
30. (Conv. → Citrate)+(RF → Citrate)+ MHR	49,824 (44,946)	47,007	17.33 (8.92)	12.67	176,000 (94,000)	4.09 (2.20)	136,000	3.11	4.2	54.4	19.7	78.3	90.7
31. (Conv. → Citrate) + (MHR → Citrate)+RF (O_2 Enrichment)	50,035 (45,310)	47,290	16.97 (8.47)	12.44	164,096 (82,096)	5.30 (4.51)	124,096	4.67	4.2	74.5	19.7	98.4	88.3
32. (Conv. → Citrate)+MHR + RF (O_2 Enrichment)	90,137 (85,412)	87,392	9.66 (4.74)	6.88	122,000 (40,000)	5.4 (4.0)	82,000	4.5	7.5	47.4	19.7	74.6	91.1

Table 6-6. ADDITIONAL BLENDING SCENARIOS FOR CONTROLLING SO_2 EMISSIONS FROM A NEW COPPER SMELTER PROCESSING 1,400 TPD-CONCENTRATE CONSIDERING COMBINATIONS OF ALL SMELTING EQUIPMENT OFFGASES (CONTINUED)

Blending Conditions[a]	Volume to Acid Plant		Percent SO_2 to Acid Plant		Gas Characteristic to FGD System				SO_2 Emissions From Acid Plant (Max. TPD-SO_2)	SO_2 Emissions From FGD System 90% Eff. (TPD-SO_2)	Uncontrolled SO_2 Emissions Including Fugitive (TPD-SO_2)	Total SO_2 Emissions to Atmosphere (Max. TPD-SO_2)	Percent Control Based on 840 TPD-SO_2 Input
	Maximum (Minimum) S C F M	Average (SCFM)	Max-imum) (Min)	Ave-rage	Maximum (Minimum) S C F M	Maximum (Minimum) % SO_2	Average S C F M	Average % SO_2					
33. [RF (O_2 Enrichment) → Citrate]+(MHR → Citrate)+ Conv.	124,628 (42,469)	84,548	7.29 (9.29)	7.23	83,896 (83,896)	3.31 (3.11)	83,896	3.21	10.4	34.6	19.7	64.7	92.3
34. (Conv. → Citrate)+[RF (O_2 Enrichment) → Citrate]+ MHR	48,971 (44,087)	46,146	17.63 (9.06)	12.90	163,800 (81,800)	4.43 (2.57)	123,800	3.45	4.1	54.9	19.7	78.7	90.6
35. (Conv. → MgO System)+ (FBR → MgO Syst)+ RF	132,620 (87,728)	106,538	6.39 (4.37)	5.44	145,600 (63,600)	6.00 (5.89)	105,600	5.53	11.1	75.1	20.0	106.2	87.4
36. (RF → MgO System) + (Conv. → MgO System) + FBR	88,432 (42,180)	61,670	9.76 (9.50)	9.67	176,000 (94,000)	4.09 (2.20)	136,000	3.11	7.4	54.4	20.0	81.8	90.3
37. (RF → MgO System) + (FBR → MgO System) + Conv.	146,869 (63,508)	106,188	6.18 (6.22)	5.75	77,600 (77,600)	3.56 (3.37)	77,600	3.46	12.3	34.5	20.0	66.8	92.0
38. (Conv. → MgO System)+ RF + FBR	136,829 (92,000)	110,810	6.35 (4.40)	5.42	122,000 (40,000)	5.4 (4.0)	82,000	4.5	11.4	47.4	20.0	78.8	90.6
39. (Conv. → MgO System)+ (FBR → MgO System)+ RF (O_2 Enrichment)	120,011 (75,119)	93,929	7.07 (5.10)	6.17	145,100 (63,100)	5.99 (5.87)	105,100	5.51	10.0	74.5	20.0	104.5	87.6
40. [RF (O_2 Enrichment) → MgO]+(Conv. → MgO System)+ FBR	88,411 (42,014)	61,577	9.76 (9.51)	9.66	163,800 (81,800)	4.43 (2.57)	123,800	3.45	7.4	54.9	20.0	82.3	90.2
41. [RF (O_2 Enrichment) → MgO]+(FBR → MgO) + Conv.	146,938 (63,433)	106,186	6.18 (6.22)	5.75	64,900 (64,900)	4.27 (4.01)	64,900	4.14	12.3	34.5	20.0	66.8	92.0
42. (Conv. → MgO)+ FBR + RF (O_2 Enrichment)	124,192 (79,300)	98,110	7.01 (5.10)	6.12	122,000 (40,000)	5.4 (4.0)	82,000	4.5	10.4	47.4	20.0	77.8	90.7
43. (Conv. → Citrate)+(FBR → Citrate + RF	62,276 (57,550)	59,530	13.61 (6.67)	9.73	145,600 (63,600)	6.0 (5.89)	105,600	5.53	5.2	75.1	20.0	100.3	88.1
44. (Conv. → Citrate) + FBR + RF	83,841 (79,116)	81,096	10.37 (5.12)	7.14	122,000 (40,000)	5.4 (4.0)	82,000	4.5	7.0	47.4	20.0	74.4	91.1
45. (RF → Citrate)+(FBR → Citrate)+ Conv.	124,618 (42,475)	84,546	7.28 (9.30)	7.23	77,600 (77,600)	3.56 (3.37)	77,600	3.46	10.4	34.5	20.0	64.9	92.3
46. (Conv. → Citrate)+(RF → Citrate)+ FBR	30,424 (25,556)	27,607	28.37 (15.67)	21.57	176,000 (94,000)	4.09 (2.20)	136,000	3.11	2.5	54.4	20.0	76.9	90.8

Table 6-6. ADDITIONAL BLENDING SCENARIOS FOR CONTROLLING SO_2 EMISSIONS FROM A NEW COPPER SMELTER PROCESSING 1,400 TPD-CONCENTRATE CONSIDERING COMBINATIONS OF ALL SMELTING EQUIPMENT OFFGASES (CONTINUED)

Blending Conditions[a]	Volume to Acid Plant		Percent SO_2 to Acid Plant		Gas Characteristic to FGD System				SO_2 Emissions From Acid Plant (Max. TPD-SO_2)	SO_2 Emissions From FGD System 90% Eff. (TPD-SO_2)	Uncontrolled SO_2 Emissions Including Fugitive (TPD-SO_2)	Total SO_2 Emissions to Atmosphere (Max. TPD-SO_2)	Percent Control Based on 840 TPD-SO_2 Input
	Maximum (Minimum) S C F M	Average (SCFM)	Max-imum) (Min)	Ave-rage	Maximum (Minimum)		Average						
					S C F M	% SO_2	S C F M	% SO_2					
47. (Conv. ⟶ Citrate) + (FBR ⟶ Citrate) + RF (O_2 Enrichment)	50,033 (45,307)	47,287	16.97 (8.46)	12.26	145,100 (63,100)	5.99 (5.87)	105,100	5.51	4.2	74.5	20.0	98.7	88.3
48. (Conv. ⟶ Citrate FBR + RF (O_2 Enr.)	71,141 (66,416)	68,396	12.23 (6.09)	8.78	122,000 (40,000)	5.4 (4.0)	82,000	4.5	5.9	47.4	20.0	73.3	91.3
49. RF (O_2 Enrichment) ⟶ Citrate] + (FBR ⟶ Citrate) + Conv.	124,625 (42,467)	84,546	7.29 (9.29)	7.23	64,900 (64,900)	4.27 (4.01)	64,900	4.14	10.4	34.5	20.0	64.9	92.3
50. (Conv. ⟶ Citrate) + [RF (O_2 Enrichment) ⟶ Citrate] + FBR	29,975 (25,091)	27,150	28.8 (15.92)	21.91	163,800 (81,800)	4.43 (2.57)	123,800	3.45	2.5	54.9	20.0	77.4	90.8
51. Blend MHR, RF & Conv. & Bleed Stream to MgO	107,308 (48,004)	72,766	8.0 (8.0)	8.0	181,406 (123,126)	4.27 (3.08)	156,449	3.56	8.9	71.6	19.7	100.2	88.1
52. Blend MHR, RF & Conv. and Bleed Stream to Citrate	110,930 (49,289)	74,800	8.0 (8.0)	8.0	112,625 (90,349)	4.27 (3.08)	107,837	3.56	9.3	49.4	19.7	78.4	90.7
53. Blend MHR, RF (O_2 Enrich) and Conv. & Bleed Stream to MgO	107,640 (48,014)	72,989	8.0 (8.0)	8.0	166,395 (109,340)	4.55 (3.4)	142,169	3.85	9.0	70.4	19.7	99.1	88.2
54. Blend MHR, Conv. & RF (O_2 Enr) & Bleed Stream to Citrate	111,550 (49,384)	75,375	8.0 (8.0)	8.0	98,595 (76,992)	4.55 (3.4)	93,950	3.85	9.4	46.5	19.7	75.6	91.0
55. Blend FBR, RF, & Conv. & Bleed Stream to MgO	107,453 (48,033)	73,038	8.0 (8.0)	8.0	159,204 (102,636)	4.68 (3.58)	135,254	4.0	8.9	69.6	20.0	98.5	88.3
56. Blend FBR, RF & Conv and Bleed Stream to Citrate	111,322 (49,456)	75,432	8.0 (8.0)	8.0	92,370 (70,535)	4.68 (3.58)	87,484	4.0	9.3	45.0	20.0	74.3	91.2
57. Blend FBR, Conv. and RF (O_2 Enrichment) and Bleed Stream to MgO	108,054 (48,129)	73,126	8.0 (8.0)	8.0	143,592 (88,830)	5.01 (4.01)	121,060	4.34	9.0	67.6	20.0	96.6	88.5

Table 6-6. ADDITIONAL BLENDING SCENARIOS FOR CONTROLLING SO_2 EMISSIONS FROM A NEW COPPER SMELTER PROCESSING 1,400 TPD-CONCENTRATE CONSIDERING COMBINATIONS OF ALL SMELTING EQUIPMENT OFFGASES (CONTINUED)

Blending Conditions[a]	Volume to Acid Plant		Percent SO_2 to Acid Plant		Gas Characteristic to FGD System				SO_2 Emissions From Acid Plant (Max. TPD-SO_2)	SO_2 Emissions From FGD System 90% Eff. (TPD-SO_2)	Uncontrolled SO_2 Emissions Including Fugitive (TPD-SO_2)	Total SO_2 Emissions to Atmosphere (Max. TPD-SO_2)	Percent Control Based on 840 TPD-SO_2 Input
	Maximum (Minimum) SCFM	Average (SCFM)	Maximum) (Min)	Average	Maximum (Minimum)		Average						
					SCFM	% SO_2	SCFM	% SO_2					
58. Blend FBR, Conv. and RF (O_2 Enrichment) and Bleed Stream to Citrate	112,167 (49,713)	75,648	8.0 (8.0)	8.0	78,460 (57,367)	5.01 (4.01)	74,360	4.34	9.4	41.5	20.0	70.9	91.6
59. MHR + Conv; RF Uncontrolled (Existing Standards)	165,000 (83,000)	125,000	5.30 (4.52)	4.67	-	-	-	-	13.8	-	89.1	102.9	87.8
60. FBR + Conv.; RF Uncontrolled (Existing Standards)	145,600 (63,600)	105,600	6.0 (5.89)	5.53	-	-	-	-	12.2	-	89.4	101.6	87.9

[a] All blended offgases, unless otherwise indicated, are processed in a double contact sulfuric acid plant.

[b] Blended offgases processed in a single contact sulfuric acid plant.

Table 6-7. OXYGEN TO SULFUR DIOXIDE (O_2/SO_2) RATIO FOR ADDITIONAL SCENARIOS AS PRESENTED IN TABLE 6.5

Blending Scenario Number	O_2/SO_2 Ratio[a]	>1.20[b]	<1.20[c]
1	2.74	X	
2	2.63	X	
3	2.71	X	
4	2.57	X	
5	2.50	X	
6	2.71	X	
7	2.54	X	
8	2.49	X	
9	2.19	X	
10	1.92	X	
11	1.92	X	
12	1.83	X	
13	1.77	X	
14	1.93	X	
15	1.83	X	
16	1.77	X	
17	2.99	X	
18	2.19	X	
19	1.00		X
20	1.45	X	
21	2.00	X	
22	1.64	X	
23	0.91		X
24	1.44	X	
25	2.00	X	
26	1.53	X	
27	0.28		X
28	1.20	X	
29	1.68	X	

[a] Calculated based on average gas characteristics to acid plant

[b] Desired minimum ratio for processing in a double contact sulfuric acid plant

[c] Considered too low for processing in a double contact sulfuric acid plant

Table 6-7. OXYGEN TO SULFUR DIOXIDE (O_2/SO_2) RATIO FOR ADDITIONAL SCENARIOS AS PRESENTED IN TABLE 6-5 (CONCLUDED)

Blending Scenario Number	O_2/SO_2 Ratio[a]	>1.20[b]	<1.20[c]
30	0.94		X
31	0.18		X
32	1.09		X
33	1.68	X	
34	0.92		X
35	1.00		X
36	0.67		X
37	2.00	X	
38	0.87		X
39	0.91		X
40	0.67		X
41	2.00	X	
42	0.78		X
43	0.280		X
44	0.44		X
45	1.68	X	
46	0.16		X
47	0.19		X
48	0.33		X
49	1.68	X	
50	0.16		X
51	1.07		X
52	1.16		X
53	1.09		X
54	1.21	X	
55	1.00		X
56	0.96		X
57	1.02		X
58	1.00		X

[a] Calculated based on average gas characteristics to acid plant

[b] Desired minimum ratio for processing in a double contact sulfuric acid plant

[c] Considered too low for processing in a double contact sulfuric acid plant

considered to have ratios too low for proper conversion without dilution air or oxygen. Consequently, they would not follow the strategy of this blenging section to reduce the volumes of offgases to the acid plants.

The remaining scenarios tend to reduce offgas volumes to the acid plant while increasing SO_2 concentrations and still maintaining adequate O_2/SO_2 ratios. The actual amounts depend upon the scenario in question, however, those that reduce the volumes to about 110,000 or less may be attractive from an economic viewpoint. This occurs because these volumes can be processed in one acid plant while higher volumes usually require two acid plants (assumed as current standard practice in the industry).

The gas volume flow rates and SO_2 concentrations to be processed in FGD systems are all higher than those included in Table 6-4. The exact values depend upon the scenario in question but generally are about triple those in Table 6-4.

Total SO_2 control efficiencies for these scenarios are somewhat lower than those presented in Table 6-4. The major difference in control efficiencies for scenarios in Table 6-4 and Table 6-6 is that acid plant control is over 99 percent, while FGD systems are assumed to control only about 90 percent. Thus, increasing volumes to the FGD systems while decreasing the acid plant handling capacity will markedly affect the total SO_2 control efficiency based on assumed control efficiencies.

A comprehensive cost evaluation is warranted to fully assess the economic viability of the above scenarios and those presented in Section 6.1.2. Although it is expected that some of the scenarios may be more cost-effective than the control approaches presently used, additional cost data is necessary.

The final control system choice, whether it be blending, traditional acid plant control, or new smelting technology, will be based on both economic and control capability considerations.

SECTION 7

APPLICATION TO EXISTING SMELTERS

7.1 GENERAL

The approaches used to control weak SO_2 offgas streams from new copper smelters can, in general, be applied to existing smelters. However, retrofitting of any control approach will generally introduce unique problems for each specific smelter.

As discussed in previous sections, the accepted control approach in the copper smelter industry is to send SO_2 laden offgases to a sulfuric acid plant. All smelters in the United States using reverberatory furnaces produce an offgas stream with an SO_2 concentration too low to serve as feed gas to a sulfuric acid plant. Thus, the major type of smelting equipment that must be controlled is the reverberatory furnace.

With the older smelters using multihearth roasters, an additional low SO_2 concentration offgas stream is produced. The major reason for this is that multihearth roasters and connecting duct work, currently in operation, are quite old and have many leakage points. In some cases, the duct work being used may be constructed of brick and has been in place for over 50 years. With all these leakage points and with the systems generally operating at negative pressure, the induced or dilution air that enters the system reduces the SO_2 concentration to well below the required acid plant input value. Furthermore, the increase in gas volume as a result of the infiltrating air makes control of the final offgas considerably more costly by increasing the size of any control system.

Thus, in the case of existing smelters, thare are two major types of equipment that must be controlled, the multihearth roasters and the reverberatory furnace. These are continuously operating devices and can be adapted to add-on controls, to produce low volume high SO_2 concentration streams. These streams can then be blended with converter gases. Close attention to operating of the converters including programming, offgas pickup hood design, and proper exhaust system design and operating is currently required to maintain steady feed conditions to the acid plant.

Another major problem that is encountered in some smelters when retrofit control systems are considered is the available space to place control equipment. Many smelters have equipment that is very closely spaced and in order to find room for control equipment, such as precipitators or baghouses, it is necessary to place these units some distance from the equipment to be controlled.

7.2 PROCESSING TECHNIQUE MODIFICATIONS

The major first step that must be taken by an existing smelter to approach weak SO_2 stream control from either the reverberatory furnace or the multihearth roasters is to seal up the system. This includes not only sealing leaks in the reverberatory furnace and the multihearth roasters but, even more important, leaks in the connecting duct work that transfer the gases to the acid plant. It has been estimated[58] that downstream leakage from reverberatory furnaces may easily be as much as 100 percent or more. Thus, where current typical reverberatory furnaces with leakage generate over 100,000 scfm, the reverberatory furnace system in Japan generates only 55,000 scfm after extensive sealing efforts.

The second most applicable technique, one that has been demonstrated to produce a reverberatory furnace offgas of sufficient strength for direct processing in a sulfuric acid plant, is oxygen enrichment (Section 3). The development work at the Caletones smelter in Chile (over 4 years) converted a typical green charge reverberatory furnace operation to total pure oxygen/fuel burning. This resulted in SO_2 offgas concentrations of well over 5 percent indicating that reverberatory furnace SO_2 control with a sulfuric acid plant is feasible. The increase in production, at least for that smelter, resulted in an economic advantage over conventional operation. The copper smelting industry is familiar with the handling and use of pure oxygen since this is an accepted technique for addition to converter air. Oxygen/fuel burners are available and have actually been used on an experimental basis in some reverberatory furnaces in the United States (Section 3). Since the Caletones experience was with a green charge furnace, some question remains as to the potential for control of calcine charge furnaces. Some work is currently being performed in Canada using oxygen/fuel burners with calcine charge furnaces.

Relatively smaller yet significant gains can, in some cases, be accomplished by other processing technique modifications such as elimination of converter slag return, operation at lower air-to-fuel ratio, instrumental control particularly pressure control, and continuous furnace charging. Blending of reduced volume flows that result from system sealing also may be a viable technique in particular situations. Converter scheduling and improvement of converter offgas collection systems, specifically including installation of shutoff and modulating dampers, can increase SO_2 concentration from offgases in those smelters that do not have a modern system design allowing greater blending flexibility.

7.3 FLUE GAS DESULFURIZATION SYSTEMS

The use of the lime/limestone gypsum neutralization and the magnesium oxide concentration system have been demonstrated in Japan (Section 4) for control of reverberatory furnace offgas. The gypsum producing system with lime or limestone has the advantage of removing the SO_2 in solid form that can be "thrown away" without introducing any additional pollution problems. This system may be the most logical for existing smelters to control calcine charge reverberatory furnaces because of the smaller amount of SO_2 generated compared to green charge furnaces.

The magnesium oxide concentration system generates an SO_2 stream in the 10 to 13 percent concentration range. While this obviously will allow direct processing in a sulfuric acid plant, it is still relatively low. The citrate concentration system, on the other hand, generates an SO_2 offgas stream over 90 percent concentration which considerably reduces the size of the entire subsequent gas handling system. The magnesium oxide system has had several years experience in Japan on a full-scale basis operating with smelter reverberatory furnace offgases. Conversely, the citrate system has only had pilot plant experience with metallurgical gases at smelters in the United States and in Sweden. If the choice were to be made between these two systems, the citrate system would have the obvious advantage except for the fact that actual full-scale experience is not yet available. In addition, the use of this concentrated SO_2 stream can readily allow production of liquid SO_2 or perhaps even sulfur with subsequent processes. The liquid SO_2 production would be quite simplified in using this concentrated stream.

The use of systems to produce sulfur introduces the problem of providing a reducing agent which is in all cases a fuel. The experience with coal as a reducing agent (which is the most logical in view of the current energy problem) has been demonstrated but has not been shown to be a highly efficient process.

The Cominco ammonia scrubbing system has had extensive experience under full-scale smelting conditions with low SO_2 concentration. A major problem of plume opacity is apparently one that appears to be solvable. Cominco is currently constructing equipment to solve the problem as a result of successful pilot plant testing.

Thus, several FGD systems are available with either actual full-scale operating experience at smelters or with sufficiently promising pilot testing to indicate a potential for application to specific smelters. The local conditions at each smelter will, of course, considerably influence the selection of any given system.

7.4 BLENDING

Blending of gases to generate a rich enough stream to be processed directly in a sulfuric acid plant is more difficult with existing smelters. This is primarily because of the additional weak streams particularly from the multihearth roasters. The local conditions at the smelter and the potential for minimizing in-leakage of air to the system will have a major influence on the capability for blending of gas streams. It should be noted, however, that there is a considerable range of options that must be considered to determine the optimum blending design at any specific smelter, as evidenced by the scenarios shown in Section 6.

7.5 ECONOMICS

Average values for the costs of controlling of weak SO_2 streams from existing smelters are not sufficient to determine acceptability of any given approach. It is necessary to review each individual smelter on a case-by-case basis because of all of the unique problems that occur with each smelter. For example, the installation of specific duct work, sealing problems, metallurgical conditions, and the general feed and production situation of any particular smelter will strongly influence the selection of a minimum cost approach. However, it should be emphasized that to obtain a minimum cost approach, all factors must be considered in relation to each other and to the specific local conditions. The entire smelting process, from feed constituents, either present or possible future, and their metallurgical requirements through to the potential marketing or disposal of pollution control products, must be evaluated concurrently to determine the optimum economic situation. The pollution control considerations are so extensive and influence the operation of the smelter to such a great extent, that they must be included as part of the overall copper production system to obtain or define the most economical path to follow for any specific smelter.

SECTION 8

CONCLUSIONS

The major weak SO_2 gas stream from copper smelters is the offgas generated by the reverberatory furnace. This gas concentration is too low to process directly in a contact sulfuric acid plant, the accepted sulfur SO_2 control system. Two major basic approaches have been considered and are indicated for controlling the reverberatory furnace. The first is to modify or improve furnace operating techniques to provide more favorable offgas characteristics facilitating control. The second is to introduce either neutralization or concentration systems for the weak SO_2 gas stream.

Combinations of the various control approaches discussed in this study can result in minimizing overall costs and increasing effectiveness. The major cost-effective approach appears to be sealing of all systems either with new or existing smelters to minimize offgas volumes that must be processed.

Using oxygen enrichment for reverberatory furnaces with a green charge appears to be a demonstrated technique for increasing the weak SO_2 stream to a high enough value to process directly in a sulfuric acid plant. Neutralizing the weaker SO_2 offgases with a lime or limestone system for calcine charge reverberatory furnaces also appears to be an economic approach, although only full scale green charge systems have been completely demonstrated. The magnesium oxide SO_2 concentration system has been demonstrated on a full-scale smelter and can produce gases with an SO_2 concentration of 10 percent allowing direct processing in a sulfuric acid plant. The citrate concentration system has been demonstrated on a pilot-scale with metallurgical gases indicating it can concentrate weak SO_2 streams up to the 90 percent level which provides greater economic advantages. The ammonia scrubbing system has been used with weak SO_2 streams from a full-scale smelter. The plume opacity problem encountered when using this system has been eliminated on a pilot scale and is currently being installed at full scale.

The combination of a FGD or concentration system with a sulfuric acid plant may introduce economies as far as capital costs are concerned Retrofitting any of the approaches for existing smelters must be determined on an individual local condition basis.

In general, from a technical standpoint, it can be stated that with all of the considered approaches discussed in this study that weak SO_2 offgas streams can be controlled from copper smelters. The cost and system to retrofit these approaches must be determined on a site specific basis. The cost to apply to new smelters may be of the same magnitude as the increase in cost for changing to flash smelting or some other new smelting process rather than using the conventional roaster, reverberatory furnace, and converter technique.

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APPENDIX A

MULTIHEARTH AND FLUID-BED ROASTERS

A.1 MULTIHEARTH ROASTER DESIGN AND OPERATING CHARACTERISTICS

A.1.1 INTRODUCTION

The blending of lean SO_2 gas streams from reverberatory furnaces with stronger gases from other smelting equipment to obtain an SO_2 concentration capable of direct processing in a sulfuric acid plant is one technique for increasing sulfur capture in the primary copper smelting industry. Roasters, as indicated in Section 2 facilitate the smelting process by introducing the flexibility of adjusting sulfur and impurity elimination. While fluid-bed roasters are known to emit high SO_2 concentrations (8 to 10 percent), a considerably lower value is emitted from some multihearth roasters in current United States production because of the excessive air dilution resulting from the poor condition of many units. The purpose of this section is to define realistic multihearth units. Analysis will include theoretical considerations as well as review of actual SO_2 concentrations from a number of multiherath roasters.

A.1.2 BACKGROUND INFORMATION

The conventional copper smelting process involves three individual process steps -- roasting, smelting, and converting. Roasting drives off a portion of sulfur from the charge producing calcines that yield a desired copper matte (30- to 45-percent copper) during subsequent smelting operations using the reverberatory furnaces. The converting process upgrades the matte to blister copper (98 percent).

Typically copper ores are low grade and are not economically suitable for direct smelting. Copper ore-bodies in the United States have a low overall copper content (1 percent or less). Additionally, most of the copper ores and concentrates are relatively high in sulfur content and if fused directly to matte, will form a low-grade product high in impurities. Thus, it is a common practice to concentrate these low-grade ores to produce a higher copper content (15- to 35-percent copper) material prior to roasting.[1]

A copper content of 30- to 45-percent in the matte is commonly used. A higher percent tends to result in a higher percent of copper retained in the furnace slag while a lower percent requires more oxidation of iron and sulfur in the matte during the subsequent and more expensive converting stage.[2] Thus, ore concentration and sulfur removal in the roasting operation must be controlled to put the reverberatory and converting operations in the best economical balance.

In addition to the aforementioned considerations, multihearth roasters have been indicated by some sources in the industry to be effective in removing arsenic and other impurities; hence, it is preferred for roasting concentrates that contain high concentrations of such impurities.[3,3a] Thus, multihearth roasters can, under certain conditions, be the more desirable approach for treating copper ores in the United States.

A.1.3 MULTIHEARTH ROASTERS

Figure A-1[4] shows a typical multihearth roaster which is essentially a cylindrical, bricklined vessel divided from top to bottom by horizontal brick hearth. Each hearth has one or several drop holes in the brickwork, leading to the hearth below. The drop holes are located alternately on the inner and outer peripheries of successive hearths. A central, rotating brick surfaced steel column extends vertically through the center of the roaster. On each

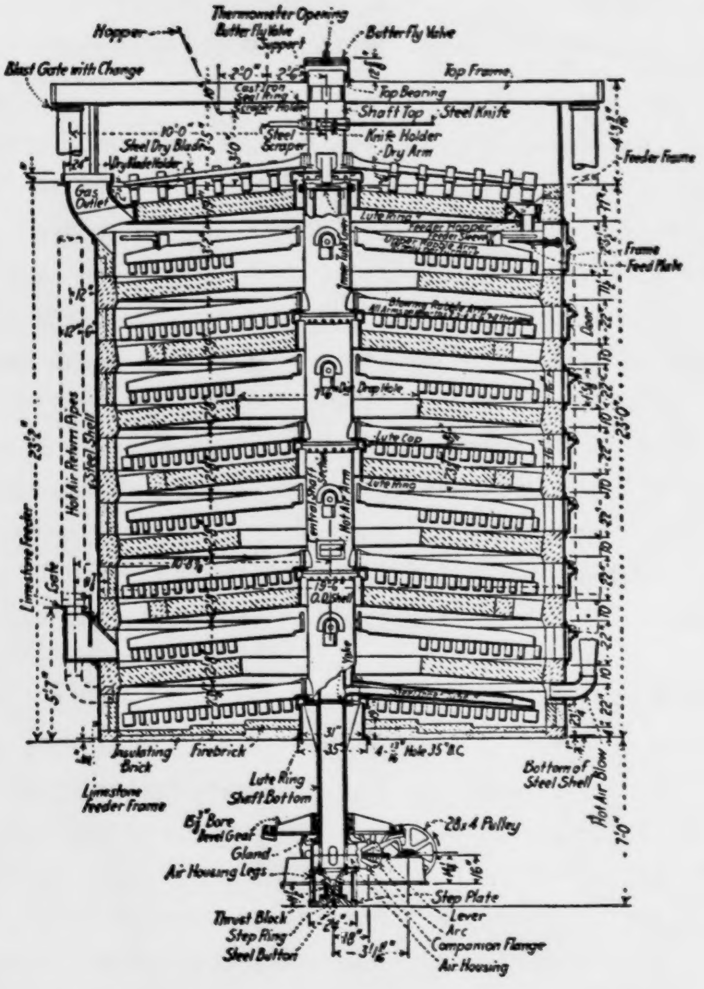
Thermometer Opening
Butter Fly Valve Support
Butter Fly Valve
Hopper
Blast Gate with Change
2'-0"
2'-6"
Top Frame
Cast Iron Seal Ring
Scraper Holder
Top Bearing
Shaft Top
Steel Knife
10'-0"
Steel Dry Blades
Steel Scraper
Knife Holder
Dry Arm
3'-0"
Dry Blade Holder
Feeder Frame
Gas Outlet
Lute Ring
Feeder Hopper
Feeder Sleeve
Frame
Feed Plate
Door
Drop Hole
Lute Cap
Lute Ring
Hot Air Arm
Limestone Feeder
Gate
Hot Air Return Pipes
Steel Shell
23'-0"
5'-7"
Insulating Brick
Firebrick
31"
35"
4-13/16" Hole 35" B.C.
Bottom of Steel Shell
Hot Air Blow
7'-0"
Limestone Feeder Frame
Lute Ring
Shaft Bottom
Bore Bevel Gear
28x4 Pulley
Gland
Air Housing Legs
Step Plate
Thrust Block
Step Ring
Steel Button
18"
3'-1/16"
Lever
Arc
Companion Flange
Air Housing

Figure A-1. Typical Herreshoff Multihearth Furnace hearth, arms equipped with rabbles are fixed to the rotating central shaft. The charge is supplied to the top hearth near the central shaft and rabbled to the periphery where it falls through the drop holes to the hearth below. The rabbles on this hearth push the feed toward the central shaft where it drops to the next hearth. This zigzag pattern continues until calcine exits from the bottom hearth.

There are several makes of multihearth roasters which differ slightly in design but all are based on the general principles of the McDougal furnace.[5] The main points of difference in construction of these multihearth roasters are the construction of central shaft, method of attaching rabble arms to the shaft, method of attaching teeth to the rabble arms, method of cooling shafts and rabbles, method of introducing air to the hearths , and number of hearths. Table A-1 lists some of the design parameters of the common roasters used in the copper smelting industry. At present practically all roasters have at least six or seven hearths with a tendency toward increasing the number to eight, nine or more. Diameters vary from 19 to 25 feet and the heights vary from 18 to over 47 feet. The central shaft not only supports the rabble arms, but contains pipes which conduct the cooling air or water to the rabble arms. Central shafts range in diameters up to 4 feet which enables a man to enter it for repairs. The speed of this shaft, which is driven by a motor and train of gears beneath the furnace, is on the order of one to two RPM. The methods of attaching rabble arms to the shaft and teeth to the rabble arms vary, but they all have the objective of easy replacement with minimum loss of time. The cooling of the shafts and rabbles are done either by water or air, with air cooling being the most common practice. The methods of air introduction vary but the main objective is to promote accurate temperature and atmosphere control to ensure proper roasting.

During roasting of copper ores it is not desirable to completely remove the sulfur in the feed because control of the matte is primarily accomplished by providing specific copper to

Table A-1. SUMMARY OF SO_2 EMISSIONS FROM MULTIHEARTH ROASTERS

Reference	Company	Type of Roaster (Number)	Number of Hearths	Dimensions of Roasters		HP	RPM	Feed Rate		Exhaust Gas		Normal Roasters in Service	Ton/SCFM (Sulfur in Feed)	Footnotes
				Height (ft)	Diameter (ft)			Tons/Day	Sulfur Percent	SCFM	Percent SO_2 (by Volume)			
1	Phelps Dodge, Douglas, Arizona	Herreshoff (24)	7	18.50^{a}	21.50	N/A	N/A	175^{b}	29 ^{b}	16,111^{c}	1.7 ^{d}	10	0.003	^{a} Value taken for standard Herreshoff roaster ^{b} Average per roaster ^{c} Average per roaster based on 10 roasters in service ^{d} Low - probably due to considerable air in leakage. Roasters arranged in double row.
2	ASARCO, Tacoma, Washington	Herreshoff (10)	N/A^{a}	25	19	N/A	N/A	250^{b}	29.5^{b}	20,000^{c}	1.5 ^{d}	5	.004	^{a} Typically 7 hearths arranged in double row ^{b} Average capacity per roaster ^{c} Average per roaster for range of 30,000 - 70,000 SCFM total ^{d} Average. Subject to air in leakage.
3	ASARCO, Hayden, Arizona	McDougal (5)	6	23.75	24	15	2	225^{a}	28 ^{b}	15,000^{c}	1.8 ^{d}	8^{e}	.004	^{a} Average per roaster ^{b} Average per roaster based on 28 percent sulfur ^{c} Average per roaster ^{d} Average based on 1.1 - 2.5 percent sulfur ^{e} Average based on 6 - 10. All but one roaster subject to air leakage. Arranged in double row.
		McDougal (3)	7	22.75	19	10	2			15,000^{c}				
		Herreshoff (3)	7	18.50	21.50	10	2			15,000^{c}				
		Bartlett-Snow Pacific (1)	N/A	34.75	25	40	2			20,000^{c}				
4	ASARCO, El Paso, Texas	Herreshoff (4)	7	N/A	22.5	N/A	N/A	250^{a}	26 ^{a}	20,014^{a}	.79	N/A	.003	^{a} Average per roaster based on maximum roast feed
5	Noranda, Quebec, Canada	Wedge (8)	7^{a}	N/A	25	15	1.09	292^{b}	24.3^{b}	20,420^{c}	5	N/A	.003	Arranged in double rows. ^{a} 7 internal and 1 external drying ^{b} Average per roaster from January 1 - June 30, 1933 ^{c} Value taken from approximate roaster treater handling 450,000 ft^3/min; therefore average per roaster based on SCFM at 1,000°F
6	Washoe, Anaconda, Montana	McDougal (56)	6	N/A^{a}	N/A^{a}	N/A	N/A	40^{b}	34 ^{b}	6,667^{c}	2.25	N/A	.002^{d}	^{a} Typically 24' diameter x 23.75' ^{b} Average per roaster ^{c} Estimation (ft^3/min) per roaster at 40 ^{d} Based on (a) 14 rows; each with 4 furnaces
7	Borg, Yugoslavia	Maguin (5)	11	47.6	21.3	N/A	1.5^{a}	200^{b}	40 ^{c}	7,560^{d}	4.6 ^{d}	N/A	.011	^{a} Average (1 - 2 RPM) ^{b} Design for each roaster ^{c} Average from test 3,5, 6 per roaster ^{d} Average from test 2,3,4,5, per roaster Tests 1 and 6 were ruled out due to fluctuations in roaster performance and feed variances.

Note: These data cover nearly an 80 year time period and should be considered as indicative of the technology and not necessarily current operations.

sulfur ratios in the calcine feed to the reverberatory furnaces. Partial roasting is characterized by oxidation of a portion of the sulfur content of the feed and a conversion of part of the iron sulfides to iron and sulfur oxides. Air is usually introduced at the bottom of the roaster and passes up through heated chambers where oxygen in the airstream reacts with iron and sulfur in the feed to liberate heat which sustains the roasting hearth temperatures. Under such conditions, the tendency is for iron sulfide to be oxidized in preference to copper sulfides and since only a partial roast is obtained, it follows that most of the copper will remain as copper sulfides or copper sulfates.

There is a limit to the amount of sulfide exposed per unit time to the action of oxygen and, therefore, to the amount of heat liberated per unit of time. If a large excess of air is used, it may absorb so much heat that there is insufficient heat available to keep the roasting ore above its ignition point (about 300°C).[6] Thus, the oxidation of sulfide minerals will cease as soon as this temperature is no longer maintained. Similarly, if there is too good a contact with oxygen, there is the possibility of the temperature rising to the melting point of the ore which excessively reduces the sulfur in the calcine product.

Additionally, temperatures affect the various chemical reactions occurring in the roaster and ultimately the SO_2 concentration in the exhaust gases. The heat of formation of sulfates is higher than that of corresponding oxides so if temperatures are low enough, sulfates will be formed with an obvious decrease in the elimination of sulfur. The equation $CuO + SO_3 \rightarrow CuSO_4$ is driven to the left at higher temperatures.[7] Thus, toward the end of the roasting step, it is necessary to maintain higher temperatures than at the beginning in order to decompose the sulfates which have a tendency to form. Figure A-2 shows the progressive removal of sulfur and the flame temperature profile for a McDougal roaster with six hearths.

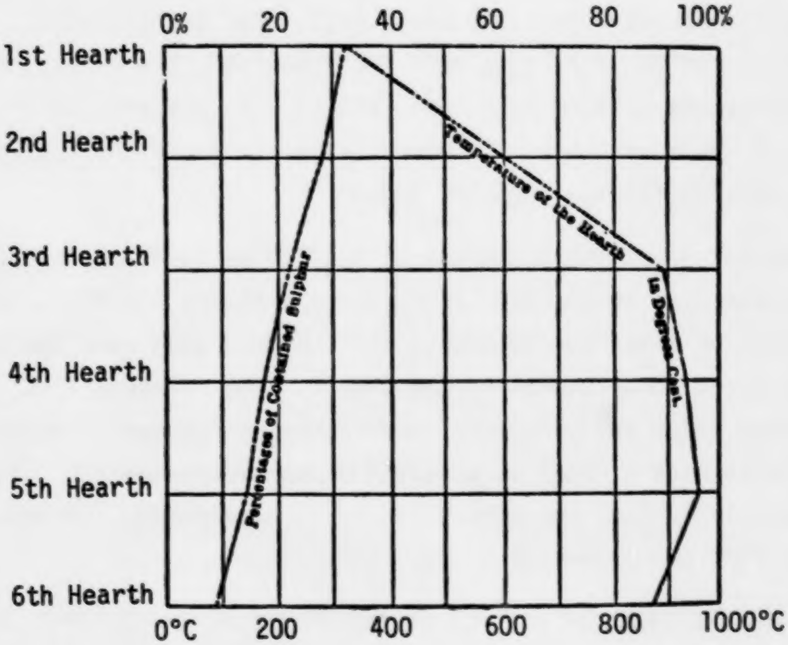

Figure A-2. Progress of Reactions and Flame-Temperature of the McDougal Roaster

A description of the roasting process is as follows:[8] "On the first hearth, ore, dropped at the circumference, and containing 6 percent of moisture, is drying out, but attains to no visible heat. Entering the second hearth it still looks dark, but shows a blue flame by the time it reaches the borders of the hearth, where it is 600°C. On the third hearth, some sparks show where the rabble passes, together with blue flame becoming hotter, with more abundant sparking, and with a flame-temperature of 900°C. On the fourth hearth, the sparking has ceased, the ore having attained an orange heat. In falling upon this hearth from the one above, the ore, as it showers down, burns freely and undoubtedly, the roasting is hastened, even by this momentary, but thorough, exposure to the ascending air. On the fifth hearth, the sulfur is leaving the ore, the discharge temperature being less than the entering one; that is, it is brighter near the outer periphery. Here the maximum temperature of 960°C is attained. On the sixth, the final, hearth heat has become uniform but lower (860°C). As the ore leaves the hearth it seems brighter, but speedily cools off to 660°C as it falls, smoking freely, into the hopper."

Current operating temperatures tend to be lower than discussed above, generally in the 550 to 700°C range during the first stages, increasing to a maximum of 800 to 850°C[10] depending upon the low melting point constituents of the charge. The strategy is to keep the charge below the sintering temperature on the upper hearths and maintain as high a heat as possible on the lower hearths. Temperatures are influenced and controlled by furnace design, air regulation, rate of feed and amount of sulfur in the ore.

Particle size and percent sulfur in the feed are known to influence roasting. Large particles roast slowly and sometimes incompletely due to limited surface area and diffusional limitations. On the other hand, fines can cause dust entrainment and roast so fast that sintering may occur. When the initial sulfur content is below 24 percent, it is necessary to finish roasting with extraneous heat.[9] The resulting exhaust gases, diluted with products of combustion, are leaner in SO_2 concentrations.

The depth of roaster bed, number and design of drop holes and number of hearths have a definite effect on the roasting process. It is assumed that about 60 percent of the sulfur removal takes place on the hearth bed while about 40 percent takes place as the ore drops through drop holes.[10] Thus, if the roast bed is too thick there will be diffusional limitations with a decrease in roasting resulting. Townsend et al.[11] investigated the roasting of lumpy chalcopyrite in an air stream at temperatures between 550°C and 750°C and followed the transformations with a microscope and microprobe. The roasted particles had an extremely porous zone of hematite covering a compact layer of magnetite. The thickness of the layers was independent of the roasting temperature. Traces of copper ferrite ($CuFe_2O_4$) were found in the hematite and were presumed to have been formed as result of establishment of a local equilibrium. Details of the transport of oxygen and sulfur through the impervious magnetite layer could not be explained. Winterharger et al.[12] found that during the roasting of copper containing pyrrhotite, various copper-iron sulfides occurred as sequential phases in the receding sulfide kernal, and copper sulfides were converted to cuprite (Cu_2O). As roasting continued (in air or in SO_2-rich gas), there was a zonal progression of these sequential phases, as would occur if the reaction rate-determining step were the gas-phase diffusion processes occurring in the pores of the roasting product. This rate-determining step has also been shown by other investigators to approximate closely the burning of iron sulfides in air.[13] The rate of oxidation appears to be determined by the rate of diffusion of gaseous reactants through the solid crust which covers the core of the sulfide particles. Chemical reaction occurs at the boundary of solid metal sulfides and metal oxides. Oxygen diffuses in; SO_2 diffuses out. Unconsumed oxygen in the gases provides the driving force. As oxidation proceeds, diffusion becomes more difficult and the reactions slow down. Additionally, at oxygen concentrations lower than about 13 percent in the gases next to the solid particles, the fire goes out. Data indicates that active oxidation of the charge requires about 13 percent oxygen in the gases and temperatures of 640° to 760°C.[14]

Drop hole area will affect the velocity of the gases in contact with falling ores. If the holes have a large area then the velocity of the gas in contact with the ore will diminish--facilitating a better roast. Since some roasting takes place during the drop from hearth to hearth it is obvious that a larger number of hearths will facilitate a more complete roast.

Some furnaces are designed with special air ports on each hearth while all furnaces have doors on each hearth which can be used in air regulation. In those furnaces with air-cooled rabble arms, air can be admitted to the hearths through holes in the arms. Another method commonly used with air-cooled rabble arms, is to use this air as preheated air for the roasting process. For these roasters the the central shaft is constructed in sections consisting of an inner, cylindrical part (cold air tube) and an outer annular part (hot air compartment). Cold air is forced in through the cold air tube and passes from here into hollow rabble arms, thus serving to keep them cool. The heated air coming from the rabble arms enters the hot air compartment, and from here it may be discharged to waste at either the top or bottom of the shaft, or admitted to hearths as preheated combustion air. It is the usual practice to admit most of the air on the bottom hearth which brings an excess of oxygen upon the ore as it is ready to leave the furnace. By the time the air reaches the upper hearth much of the oxygen has been replaced by SO_2 causing less rapid roasting of the fresh ore and consequently minimizing the danger of sintering. The hearth doors may be partly opened to supply additional oxygen to prevent sulfate formation or opened wide to allow a large excess of air to rush in and cool an overheated charge.

Temperatures are ideally set from 600° to 700°C during the first stages of roasting and increase to 800° to 850°C by the final stages.[15] The strategy is to keep the charge below the sintering temperature on the upper hearths and maintain as high a heat as possible on the lower hearths. The need to remove arsenic from some concentrates calls for consideration of the temperature to which the solids should be heated during the roast. Among the arsenic sulfides that may be present in copper ores are $FeSAs_2S_3$, As_2S_3, and As_2S_5. The As_2S_3 boils at 707°C, while As_2S_5 sublimes at 500°C with decomposition. Arsenic trioxide melts at 310°C and boils at 475°C.[6] Thus, a portion of the arsenic will be volatilized at operational temperatures within the roaster. Also, the amount of oxygen present affects arsenic removal. As_2O_3 is preferred since it is quite volatile and will pass off with the roaster gases; however, in an oxidizing atmosphere, much of the arsenic will oxidize to As_2O_5 which is less volatile and form stable, nonvolatile arsenates with other metallic oxides. Usually, it is necessary to alternate oxidation and reduction several times to completely remove arsenic. A similar phenomenon applies to antimony which goes from Sb_2O_3 to Sb_2O_5 in an oxidizing atmosphere. Thus, roasting can be ideally controlled for some impurity removal through proper temperature and air regulation.

Finally, typical roasters handle from 125 to 150 ton/day using high sulfur charge. If copper is high in the charge the capacity may be increased since less roasting is required (i.e., there is more sulfur left in the product). Roasters can handle up to 350 ton/day.[17,18]

A.1.4 SO_2 EMISSIONS FROM MULTIHEARTH ROASTERS

Table A-1 lists data obtained from several multihearth roasters in the United States and one from Yugoslavia.[19,20,21,22,23,24,25] These data indicate that the SO_2 concentrations (by volume) vary from less than 1 to 5 percent. It should be noted that roasters 1 to 4 in Table A-1 were reported to have considerable air leakages which would result in low SO_2 offgas concentrations.

Additionally, roasting eliminates a portion of sulfur in the feed which is based on the required Cu/S ratio for the subsequent smelting operations. Thus, if a feed contains a small percent copper and another feed contains a larger percent copper, then in order to obtain the same Cu/S ratio for both feeds, a larger percent of sulfur must be eliminated in the former. Roasters 2 and 5 in Table A-1 had a feed copper content of 22.8 and 5 percent, respectively. Thus, to obtain similar Cu/S ratios, it is apparent that roaster 5 had to eliminate more sulfur indicating a more complete roast and a subsequent higher SO_2 concentration. Nevertheless, average SO_2 concentrations of 4 percent by volume have been reported for multihearth roasters in the United States.[26,27]

An accurate calculation of the oxygen consumed for any specific roasting case requires knowledge of the mineralogical character and degree of transformation of the particular charge. However, a general formula for estimation of oxygen consumption using the predominant chemical, metallurgical, and thermodynamic aspects of the process has been proposed.[28]

Table A-2 lists the mineral conposition of the roaster charge for the Bor and Majdanpek ore concentrates and the quantities of the minerals in the calcine produce therefrom. The aforementioned reference (28) calculated heat balances based on reactions considered to be most significant for the Bor roaster. The accuracy of the calculated results depends upon accuracy of the required input data; the weight fraction of components in the calcine; the fraction of dissociable sulfur and arsenic (or other minor elements) actually removed; and the fraction of copper oxidized. The results are shown in Tables A-3 and A-4. These calculations were based upon data for the Bor, Yugoslavia roasters. It was also assumed that the ratio:

$$\frac{FeS_2 \text{ to } Fe_3O_4}{FeS_2 \text{ to } Fe_2O_3}$$

is constant over a broad range of sulfur removed in the offgas, that the fraction of copper oxidized was about 0.8 the ratio of sulfur removed by dissociation/dissociable sulfur in charge, and the fuel oil was assumed to contain 1 percent sulfur and provide about 150,000 Btu/gallon when burned with 15 percent excess air. Additionally, these values for SO_2 concentrations may be somewhat lower for charges containing significant quantities of Sb, Pb, Bi, and Zn since, theoretically, these compounds can affect the heat balance and subsequent gas SO_2 concentrations primarily because their elimination requires oxygen. The conclusion reached in the study was that the SO_2 concentration in exit gases from multihearth roasters can be held above 5 percent provided at least 6 percent of the sulfur is removed from the charge. Also maintaining this concentration level requires monitoring the

Table A-2. MINERAL COMPOSITION OF ROASTER CHARGE AND CALCINE, CLEAN CONCENTRATE[28]

Mineral Components	Kkg per 100 kkg of Charge	
Clean Charge	In Charge	In Calcine
FeS_2	25.18	1.05
$CuFeS_2$	49.01	
ZnS	1.52	
Inerts	24.29	24.29
FeS		6.78
FeO		0.21
Fe_3O_4		2.31
$CuFeS_2$		32.28
$CuOFe_2O_3$		21.83
ZnO		1.27
Total	100	90.02

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Table A-3. THERMAL CALCULATIONS, CLEAN CHARGE BASIS: 1 KKG DRY CHARGE; 25°C: EXIT GAS ≥200°C: EXIT CALCINE 740°C. WATER CONTENT OF CHARGE: 9WT PERCENI: RADIATION PLUS COOLING LOSSES, 15 PERCENT

Fraction sulfur removed	0.1	0.2	0.3	0.35	0.4	0.539	0.65
Sulfur removed, kg/kkg	31.05	62.1	93.15	108.7	124.2	167.4	201.8
Ht in calcine, kcal/kkg	152452	147567	142602	144064	143522	141620	140281
Ht in water, kcal/kkg	63445	63445	63445	63445	63445	63445	63445
Wt of exit gas, kg/kkg	342	684	1026	1368	1618	2312	2866
Ht in exit gas, kcal/kkg	11633	23265	34897	57471	67957	97108	120388
Total ht absorbed, kcal/kkg[a]	261659	269418	277087	304728	316164	347500	372732
Ht of reaction, kcal/kkg	−51037	−101872	−163032	−255767	−327306	−526183	−684997
Ht deficiency, kcal/kkg[b]	210621	167546	114055	48959	−11142	−178682	−312266
Required inlet gas temp at balance, °C	785	527	162	66	...	...	...
Oil required, kg/kkg	20.5	18.3	11.1	4.8	...	...	...
Excess exit gas, kg/kkg	400	317.9	216.5	93.6	...	...	...
Total exit gas, kg/kkg	742	1001.9	1242.5	1461.6	1618	2312	2866
Total SO_2 in exit gas, kg/kkg[c]	62.5	124.5	186.5	217.5	248.4	334.8	403.6
Exit gas % SO_2: wt (vol)	8.4 (3.9)	12.4 (5.8)	15.0 (7.2)	14.9 (7.1)	15.4 (7.4)	14.5 (6.9)	14.1 (6.7)
Exit gas % SO_2: wt (vol) in absence of fuel burning	18.2 (8.9)	18.2 (8.9)	18.2 (8.9)	15.9 (7.6)	15.4 (7.4)	14.5 (6.9)	14.1 (6.7)

[a] Includes 15% heat loss. [b] Total heat absorbed + heat of reaction. [c] 2 × sulfur removed + 0.02 × kg oil/kkg.

Table A-4. THERMAL CALCULATIONS, HIGH ARSENIC CHARGE BASIS: 1 KKG DRY CHARGE: 25°C; EXIT GAS ≥200°C: EXIT CALCINE 740°C. WATER CONTENT OF CHARGE: 9 WT PERCENT; RADIATION PLUS COOLING LOSSES 15 PERCENT

Fraction sulfur removed	0.063	0.1	0.2	0.3	0.4	0.5
Sulfur removed, kg/kkg	19.4	30.75	61.5	92.25	123.0	153.8
Ht in calcine, kcal/kkg	149459	142597	138261	133564	133120	128279
Ht in water, kcal/kkg	63445	63445	63445	63445	63445	63445
Wt of exit gas, kg/kkg	590	601	785	1597	1789	2283
Ht in exit gas, kcal/kkg	20072	20442	26697	54363	75133	85902
Total heat absorbed, kcal/kkg[a]	267923	260872	262663	289079	312452	330770
Ht of reaction, kcal/kkg	−163372	−103489	−122627	−270187	−411881	−553575
Ht deficiency, kcal/kkg[b]	104551	157383	140036	18891	−99429	−222804
Required inlet gas temp at balance, °C	227	362	245	41	...	...
Oil required, kg/kkg	10.2	15.2	13.6	1.9	...	...
Excess exit gas, kg/kkg	198.9	296.4	265.2	37.1	...	...
Total exit gas, kg/kkg	788.9	897.4	1050.2	1634.1	1789	2283
Total SO_2 in exit gas, kg/kkg[c]	39.0	61.8	123.3	184.54	246	307.6
Exit gas % SO_2: wt (vol)	4.9 (2.2)	6.9 (3.1)	11.7 (5.5)	11.3 (5.3)	13.8 (6.5)	13.5 (6.4)
Exit gas % SO_2: wt (vol) in absence of fuel burning	6.6 (3.0)	10.2 (4.8)	15.7 (7.5)	11.6 (5.4)	13.8 (6.5)	13.5 (6.4)

[a] Includes 15% heat loss. [b] Total heat absorbed + heat of reaction. [c] 2 × sulfur removed + 0.02 × kg oil/kkg.

exit gas O_2 concentration and controlling it at 12 percent along with controlling heat losses to a maximum of 15 percent and calcine exit temperatures to a maximum of 1,364°F.

A.1.5 CONCLUSIONS

Based on actual SO_2 offgas emissions (see Table A-1), multihearth roasters are capable of releasing SO_2 concentrations up to 4 percent volume. Likewise, the above study indicated that at least 5 percent SO_2 (up to 7 percent) offgas concentration can be maintained provided:

1. At least 60 kg of sulfur is removed per kkg charge
2. Exit gas O_2 concentration does not exceed 12 percent (assuming oxygen is supplied by air addition with consequent increase in the accompanying nitrogen dilution effect)
3. Controlling heat losses to a maximum of 15 percent
4. Controlling the calcine exit temperature to a maximum of 740°C

The SO_2 concentration will vary depending on the amount of sulfur contained in the ore and the actual operating parameters. Nevertheless, a 5 percent SO_2 offgas concentration seems feasible in discussing the capabilities of the multihearth roaster.

Additional means may be employed to upgrade the SO_2 concentration from multihearth roasters. These points may be summarized as follows:[29]

1. Operate with the lowest oxygen concentration consistent with smelter calcine requirements
2. Drying in a separate operation
3. Better insulation and recovery of heat from rabble-arm cooling air
4. Preheat incoming air
5. Keep exit calcine temperatures lower
6. Modification: reduce air infiltration to a controllable level; effect control through the use of oxygen monitors in the exit gas duct.

A.2 FLUID-BED ROASTER DESIGN AND OPERATING CHARACTERISTICS

Fluid-bed roasting involves the autogenous oxidizing of sulfide particles while they are suspended in an evenly distributed stream of air. It is based upon the principle that the blowing of air through a bed of fine solids tends to support the particles at moderate velocities. These particles may be permanently suspended in an expanded or fluidized bed. The particles are essentially surrounded by air so that rates of gas/solid roasting reactions are high. The reactions occurring are similar to those occurring in multihearth roasters (refer to Appendix A.1).

Figure A-3 shows a cutaway of a typical fluid-bed roaster. Air is blown into the roaster by means of a tuyere plate at the bottom, and concentrates are added in particulate or slurry form near the top of the roaster. The roasting operation is begun by heating the roaster (usually containing an inert bed of sand or calcines) to the temperature at which the concentrate will ignite by air. The temperatures are maintained between 930° and 1,300°F. The concentrates are then added, slowly at first to begin the roasting and to make the operation autogenous.

Reaction rates within the roaster are rapid and an important consequence is the high efficiency of oxygen utilization by the roasting reactions. This leads to air requirements only slightly in excess of the stoichiometric amount. SO_2 concentrations in the effluent roaster gases are considerably higher than those of the multihearth roaster. It is 8 percent compared to 4 percent (new units

Figure A-3 shows a cutaway of a typical fluid-bed roaster. The fluidized state is accomplished by considerable agitation of the particles in the bed which results in efficient heat transfer and a uniform temperature across the roaster. This, in turn, permits accurate control of the roasting temperature.

One problem, however, caused by the high chemical efficiency of the fluid-bed is that the roaster tends to overheat due to the

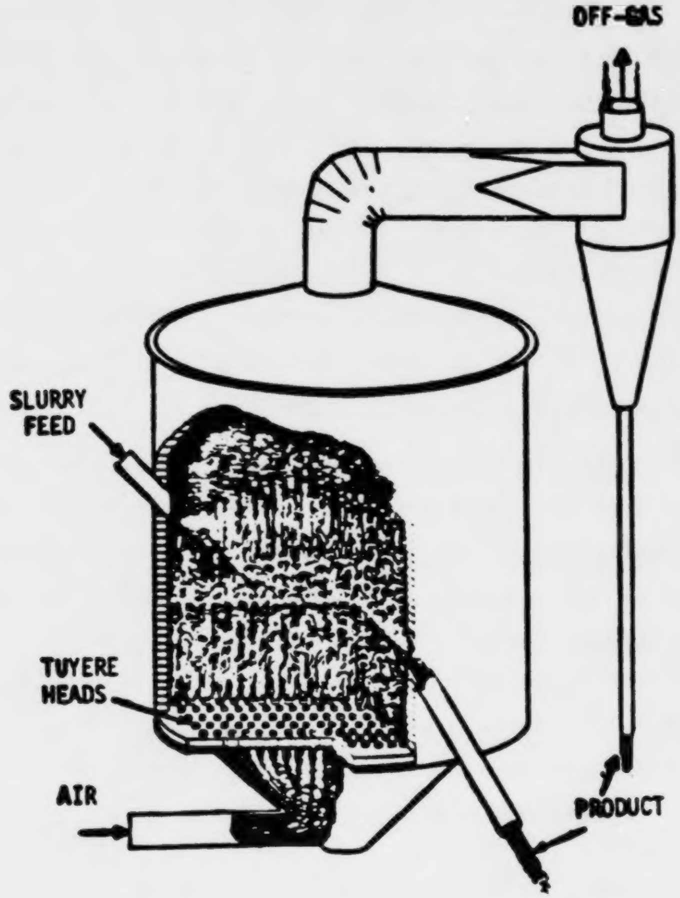

Figure A-3. Typical Fluid-Bed Roaster[1] (Text)

exothermic oxidation reactions. This could result in sintering, overoxidation, or agglomeration which could collapse the bed. This problem is generally rectified through the addition of water or inert fluxes (for use in subsequent smelting) with the concentrates.

During copper roasting, a major portion of the fluidized solids are carried out through the top of the roaster. These are collected in cyclones above the roaster while the remainder of the solids overflow the fluid-bed portion of the roaster. Thus, the bottom portion of the roaster contains a stable fluid-bed in which the larger particles are oxidized. In design, the larger particles which require lengthy oxidation times have a long residence time in the stable bed portion, while smaller particles are blown out before they have time to overoxidize. Thus, the fluid-bed roaster offers a means of producing an even roast.

A critical factor in fluid-bed roaster design is that the largest particles in the concentrate must become fluidized, thus preventing tuyere clogging and eventual collapsing of the bed. Hence, the velocity of the gas must be considered of prime importance in actual operational practices.

The residence times of particles control, in part, the extent of the oxidation reactions taking place. The residence times are controlled by varying the depth of the stable bed, the rate of concentrate feed, and air flow rate.

Advantages of fluidized roaster over conventional multihearth roasters include:

1. Roaster offgases are ideal for making sulfuric acid since the roaster operates under continuous steady state conditions with a relatively high SO_2 concentration in the offgas.
2. Offgas volumes are reduced significantly due to reduced air requirements.
3. Reduced residence time and consequently fewer pieces of equipment needed for the same production.

While it appears that the current philosophy in the copper industry is to use fluid-bed roasters, some problems may exist that would inhibit their use. Fine grind is needed and with underground ores it might be necessary to reduce the size so much that the grinding costs could be excessive. Also, there may be an increase in magnetite formation depending upon the composition of the charge. Finally, there is some concern over problems with impurity removal due to the decreased residence time within the roaster.

Fluid-bed roasters are reported to be undesirable for processing concentrate ores containing high impurity levels.[30] These impurities are relatively difficult to separate by volatilization, and a fluid-bed roaster may not provide sufficient residence time for complete separation. However, this is entirely dependent upon the impurities and their concentrations in the feed. Multihearth roasters, on the other hand, provide a much longer residence time as the ore travels through each hearth.

In a recent study, it was found that the amount of arsenic volatilized in the roaster and furnace combined appear to be the same for both the fluid-bed roaster-reverberatory furnace combination and the multihearth roaster-reverberatory furnace combination, although the fluid-bed roaster volatilizes less arsenic than a multihearth roaster for a given set of conditions.[31]

Although the multihearth roaster is capable of removing more arsenic than a fluid-bed roaster, a fluid-bed roaster is being used at the Anaconda smelter where the feed input is high in arsenic content. This is contrary to the belief that fluid-bed roasters should not be used when the arsenic content in smelter feed is high. However, the Anaconda fluid-bed roaster, in conjunction with an electric furnace, produces a matte grade above 50 percent. The choice of the type of roaster used with a "high" arsenic content feed does not seem to be governed by the high amount of arsenic in the feed, but by the quality of matte desired from the smelting furnace. Since multihearth roasters seem to yield calcine which produces a lower grade matte than fluid-bed roasters for any given amount of arsenic elimination, they tend to be preferred whenever the above two qualities are desired simultaneously. This is particularly true when lead and antimony are present. Complete proof of the above observation has not been established.

Nevertheless, fluid-bed roasters warrant consideration for weak stream SO_2 control since the blending of fluid-bed roaster, reverberatory furnace, and converter offgas has been reported feasible and produces a considerably higher combined SO_2 concentration.[32]

APPENDIX B

REVERBERATORY FURNACE HISTORY, DESIGN AND OPERATION

B.1 FURNACE FUNCTION

The primary function of the reverberatory furnace is to economically smelt the required copper-bearing charge into a molten mass. The objective of the furnace operation is to produce separate fluid layers of lower specific gravity discardable slag (iron-gangue comprising the top of the bath) and a higher specific gravity matte (consisting theoretically of a mixture of $Cu_2S \cdot FeS$ comprising the lower fluid layer). The matte can be separated by selecting tapping levels. It is then further treated in other furnaces for separation of Cu from the Fe and S. The slag is tapped from the furnace at a higher level and usually discarded.

B.2 BRIEF HISTORY

Previous to the development of the first reverberatory in America at Colorado Smelting and Mining Company in Butte, Montana in the year 1879,[33] most smelting was done in blast furnaces. The ore content of oxides and pyrites, available at that time, were more readily processed in blast furnaces. With sulfide ores becoming more prevalent, the reverberatory furnace became the more efficient processing device. The first reverberatory furnaces were of the batch type and the charge was smelted by grate-burning of wood or charcoal. From the first small 10 ton per day batch furnace, size gradually increased up to lengths of 50 meters (160 feet) and widths of 11 meters (36 feet). As heat loss increased with the area of refractory arch and side-wall surfaces, the largest furnaces proved less economical, and present-day dimensions are slightly over 30 meters (100 feet) in length and 8.5 to 10.4 meters (28 to 34 feet) in width in most instances.

B.3 MODERN CONSTRUCTION

Reverberatories are large horizontal chambers constructed of refractory material throughout, capable of being fired through one end and containing an outlet flue at the opposite end to allow exit gaseous products of smelting and combustion.

There are two types of roofs or arches in current use as illustrated in Figure B-1. The original arch-type is constructed of silica brick and is sprung between skews and buckstays at the sides so that it is suspended in its entirety, independent of the walls or ends. The original arch thickness is 0.51 meters (20 inches) and is maintained by slurring[34] on the underside through a nozzle and a pipe connected to a Quigley-type gun. Ribs above the original arch are sometimes installed so that an upper or relieving arch may be installed above the original, when it becomes thin. The maximum allowable width of a sprung arch is about 8.5 meters (28 feet) due to inherent brick strengths.

The second and newer type of arch is made of brick individually suspended by means of hangers attached to the brick and to the superstructure. Refractories may be of either silica or basic brick. This type of arch is generally panelized[35] into relatively small removable sections (typically 3 by 10 feet) bound together with new panels which can be done in as short a time as a half hour. Individual brick or pairs may also be replaced without being part of the panel. The principle advantage of suspended arches is that any width of arch may be used and cross-sections can be installed at different elevations to allow any desirable internal contouring. There generally is a much greater heat loss through an arc constructed of basic material, but bricks wear longer under furnace conditions. The modern trend is towards the use of basic suspended arches.

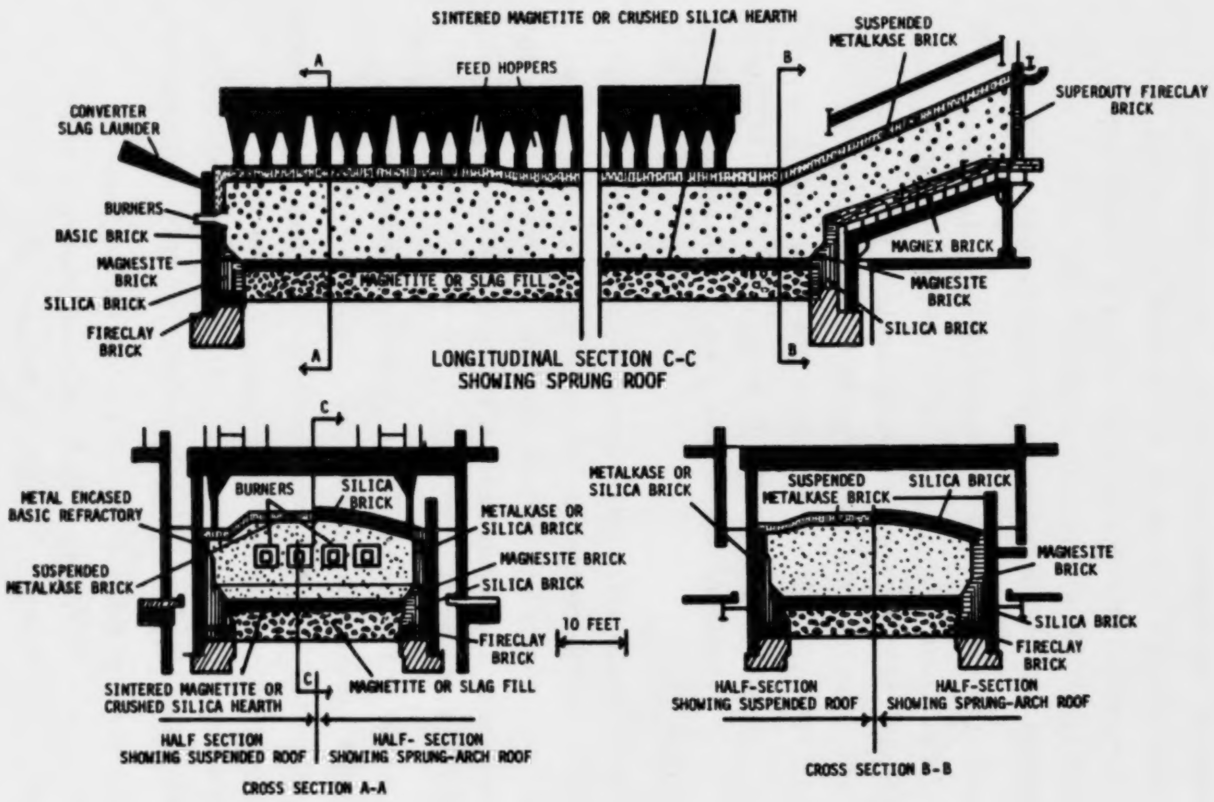
SINTERED MAGNETITE OR CRUSHED SILICA HEARTH
FEED HOPPERS
SUSPENDED METALKASE BRICK
SUPERDUTY FIRECLAY BRICK
CONVERTER SLAG LAUNDER
BURNERS
BASIC BRICK
MAGNESITE BRICK
SILICA BRICK
FIRECLAY BRICK
MAGNETITE OR SLAG FILL
MAGNEX BRICK
MAGNESITE BRICK
SILICA BRICK
A
A
B
B
LONGITUDINAL SECTION C-C SHOWING SPRUNG ROOF
C
C
METAL ENCASED BASIC REFRACTORY
BURNERS
SILICA BRICK
METALKASE OR SILICA BRICK
MAGNESITE BRICK
SILICA BRICK
SUSPENDED METALKASE BRICK
FIRECLAY BRICK
10 FEET
SINTERED MAGNETITE OR CRUSHED SILICA HEARTH
MAGNETITE OR SLAG FILL
HALF SECTION SHOWING SUSPENDED ROOF
HALF- SECTION SHOWING SPRUNG-ARCH ROOF
CROSS SECTION A-A
METALKASE OR SILICA BRICK
SUSPENDED METALKASE BRICK
SILICA BRICK
MAGNESITE BRICK
SILICA BRICK
FIRECLAY BRICK
HALF-SECTION SHOWING SUSPENDED ROOF
HALF-SECTION SHOWING SPRUNG-ARCH ROOF
CROSS SECTION B-B

Figure B-1. Typical Reverberatory Furnace Design for Copper-Matte Smelting Showing Sprung & Suspended Arch[9]

The sprung silica arch would remain on a furnace practically forever, with the excellent continuous hot strength of silica, if it were not affected by splashed matte and slag and the corrosive fumes of the furnace atmosphere. Unfortunately, the chemically acid silica brick can be quite readily corroded by the primary iron-silicate and iron-lime-silicate constituents of the furnace fumes and slags. The continual use of silica spraying furnaces has prolonged their life to as much as 12 years.

The magnesite-chrome system of refractories (basic brick) offers significant improvements in roof life with the typical iron and iron silicate slags of the reverberatory furnace but is more expensive. However, the hot strength of basic brick is much less than silica. This coupled with the permanent expansion characteristic of basic brick, makes it unsuitable for traditional sprung arch construction; therefore, a suspended system must be used on most reverbs.

The grade of basic brick most commonly used is the chemically bonded type with an MgO content of 40 to 60 percent. The shapes are normally steel encased to reduce spalling. The steel is also thought to form complex compounds with refractory-iron ingredients that are beneficial to brick life.

Direct bonded and rebonded fused grain basic refractories are premium type products which can give increased performance in the high wear area of the reverb roof and have come into general use in certain areas -- usually in the smelting zone from 10 to 40 feet beyond the burners. However, their increased cost should be economically justified by careful analysis of their performance.

Their are various types of brick suspension as shown in Figures B-2a through B-2d. The first and most common involves suspension from rods hooked into tops of bricks, usually using one rod for two brick. A more recent innovation involves suspension of brick by interlocking with a refractory to which the suspension rod is attached.

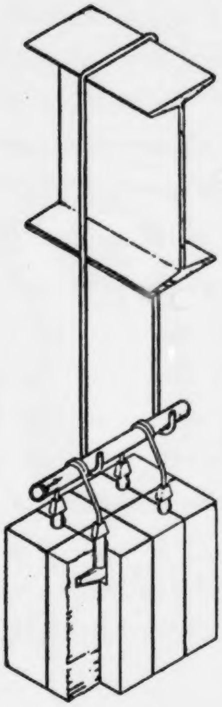

Figure B-2a
Typical Tile Support System

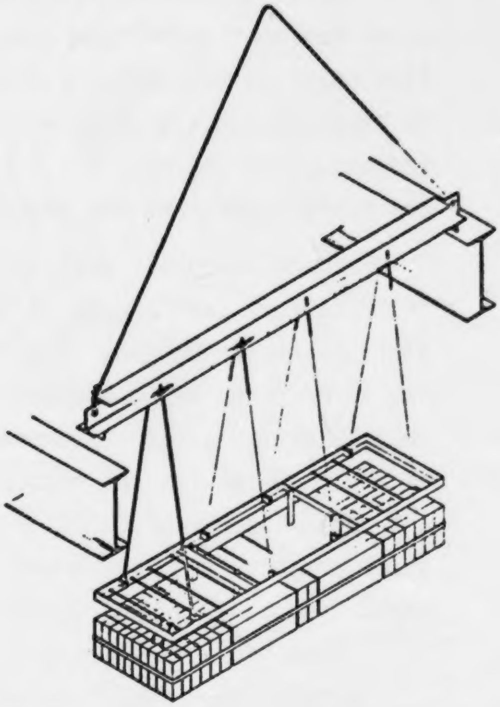

Figure B-2b
Panel Construction

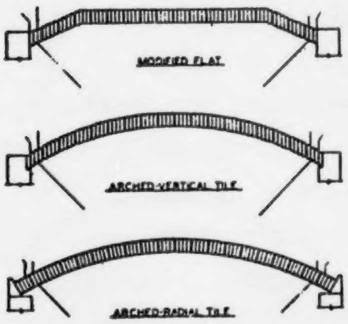
MODIFIED FLAT
ARCHED-VERTICAL TILE
ARCHED-RADIAL TILE

Figure B-2c

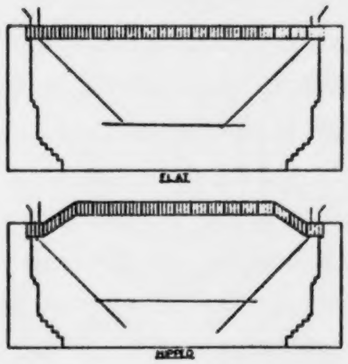
FLAT
HIPPED

Figure B-2d

Typical Roof Cross Sections

Figure B-2. Suspended Arch Brick Assembly and Mounting Design

Sectionalizing of brickwork into panels is now commonly practiced in the smelting zone. It is claimed that an average time required to replace a 3 by 10 foot panel is about a half hour as compared to several hours to replace a similar area with individual or paired brick. Replacement panels are prefabricated and bound beforehand and effect a saving in hangers required.

Furnace sidewalls are constructed of refractory material in brick form that may be of silica, clay or basic material although the basic type is generally used on the inner face of the furnace and below the bathline. Walls may be corbelled (bricks set so as to form short supporting brackets) because of the temperatures and liquid attack beneath the bath line and under the burners. Water or air cooled jackets of copper, steel, or cast iron are generally used around tap holes, skim bays, bridge walls and, in the deep bath furnace, generally all along the entire bath line.

External insulation of the brickwork has been tried but is not extensively used as fusing and melting of the internal face of the brickwork is greatly increased with its use.

Most furnace bottoms rest upon a tamped sand, clay, or concrete base of several feet thickness. On this base will be layers of magnetite-slag, chrome ore, quartz, converter slag, used in combination or singly, and all fused into place. Eventually bottom thicknesses are several feet deep, the final thickness being determined by type of furnace, desired bath depth and temperature and peculiarities of the charge to be smelted. Bottom cooling may be accomplished by means of air piped under or through the bottoms or just above the foundations. Typical furnace across sections are shown in Figure B-3.

Most of the actual smelting is done in the first 70% of the furnace length, allowing almost complete separation of the matte and slag layers in the balance of the furnace length. The most intense smelting zone is usually about 15 to 20 feet from the burners and temperatures[36] will range from 1500°C (2800°F)

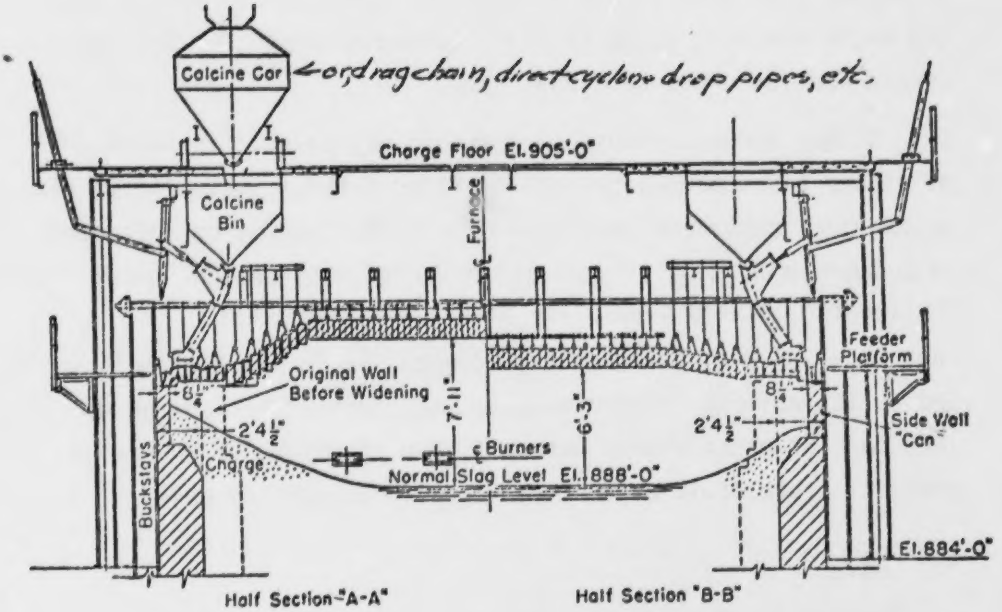
Calcine Car
← or, drag chain, direct cyclone drop pipes, etc.
Charge Floor El. 905'-0"
Calcine Bin
Furnace ℄
Feeder Platform
Original Wall Before Widening
$8\frac{1}{4}$"
$2'4\frac{1}{2}$"
7'-11"
6'-3"
$8\frac{1}{4}$"
$2'4\frac{1}{2}$"
Side Wall "Can"
℄ Burners
Charge
Normal Slag Level El. 888'-0"
Buckstays
El. 884'-0"
Half Section "A-A"
Half Section "B-B"

Figure B-3. Transverse Half Sections of Furnace[9] to 1700°C (3100°F) in this area. Bath temperatures in the furnace will range from 1300°C (2300°F) down to 1100°C (2100°F), usually near the skim bay. As the slag forms in the top layer of the bath, it receives more heat reflected from the flame and the arch and is the hottest portion of the bath. It also serves, undesirably, as a protective barrier for heat transfer to the matte layer beneath. The height of the furnace arch above the bathline is determined by the heat and combustion requirements of the smelting, plus heat losses through the refractories and in slag and matte removal, so as to allow approximately 1,000 Btu per square foot of cross-sectional area.

Either sprung or suspended arches may be used in furnaces of either side-charged or bath smelting types. Installation plus maintenance costs are comparable for either sprung or suspended arch types and, today installation would be between $4 and 5 million for a furnace complete with auxiliaries. The advantages of the reverberatory furnace lie in its flexibility and in its ability to handle up to 1600 tons of hot charge or 1200 tons of green charge per day. Use of oxygen or preheated combustion air would raise these capacities considerably.

B.4 FUELS

Originally, wood or charcoal was the only fuel used, but in the early 1900's coal came into prominent use, being first burned on grates and later pulverized and blown into the furnace with pressurized air. This was gradually replaced by oil fuels in the 1920's,and in the 1930's the use of natural gas firing became most common. With the shortages of natural gas in the early 1970's, all plants are reverting back to some oil firing and many are planning on eventually returning to the use of pulverized coal. Gaseous fuels give a clear nearly invisible flame, oil fuels produce a semi-luminous flame and pulverized coals produce a luminous flame.

With the rapidly developing energy shortage, the only large reserve of fossil-fuel energy in the United States is coal, so it is inevitable that coal will be the furnace fuel of the future. Its use gives a much more luminous flame than does oil or gas and the heat transfer from flame to charge is thought to be more efficient. The two main disadvantages of its use is that it must be finely pulverized just before use, and the presence of fly ash after its combustion may either form a thin insulating blanket on the furnace bath and/or contaminate the gases with additional particulate matter that is hard to remove.

B.5 FURNACE BURNERS

A vast conglomeration of burner types and positions have been used in various reverberatories in past installations. Most of the "odd-ball" burners have fallen by the wayside, and the use of standardized main burners through the bridgewall (using only pressurized primary and secondary air for idealized combustion) is now becoming almost universal.

Burners must be large enough and numerous enough to supply the heat necessary to smelt the tonnage of charge desired--insofar as cross-sectional area is available for proper combustion. The trajectory of the flame from each burner must be such that the maximum heat is transferred directly to the charge and a minimum to the furnace arch. The use of a combustion chamber upstream of the furnace has generally been abandoned as uneconomical. The judicious use of oxy-fuel burners through the arch is becoming more prominent and this is desirable to "level-out" the temperatures in the charge smelting zone.

In general, furnaces are equipped with five to eight main burners through the bridge-wall and the ports are usually jacketed to protect both burners and wall. Each burner is capable of slight adjustment (movement) to direct its flame in the desired trajectory. Proper mixture of fuel and air is essential at all levels of burner capacity.

B.6 FURNACE CHARGING CONFIGURATION

There are two types of reverberatories in current use and they differ principally in the amount of bath and the method charging.

The first type in use, and still extensively used, is the deep-bath furnace, wherein a molten bath of several feet depth is maintained throughout the furnace, covering the entire bottom. The charge may be admitted to the furnace by dropping through the arch, through retractable or fixed charge guns, discharging through ports in the sidewalls which extend some distance towards the middle of the furnace, or in one instance through green charge slingers that cover the entire bath in the smelting zone. A calcined charge must be used through charge guns or through arch drop holes in the center or along the furnace sidewalls. Green charge may also be dropped through the arch or introduced through belt slingers. In all cases, every effort is made to distribute the charge on top of the deep molten bath in the smelting area, to expose the largest possible area to the heat from the burners and the arch. Water or aircooled jackets in the sidewalls are used because the molten bath is in direct contact with the sidewalls.

The second type is the side-charged furnace, (see Figure B-4) which is more predominately in use today and usually has a bath depth of three feet or less. Basically, the green or calcined charge is dropped through the arch along the walls to form banks of material that slowly melts, giving sufficient protection to the sidewalls to generally eliminate special cooling requirements. The smelted material forms a liquid bath throughout the center length of the furnace. It is adaptable for either calcine or green feed charging or a combination of both. Typically, feed is gravity-charged into hoppers staggered along each side of the furnace and located above drop holes through the arch, a few inches in from the sidewalls. The hoppers may be fed by calcine car discharge, drag chain distribution of calcine or green feed, or by conveyor

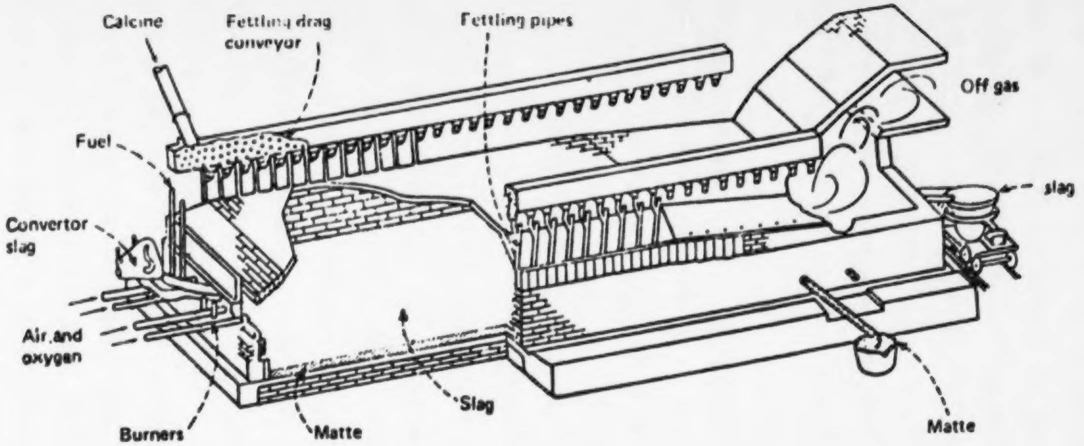
Calcine
Fettling drag conveyor
Fettling pipes
Off gas
Fuel
slag
Convertor slag
Air and oxygen
Burners
Matte
Slag
Matte

Figure B-4. Side-Charging Calcine by Drag Chains Green Feed Can be Fed in Same Manner[1] (Text) belt and tripper car for green feed. As the angle of repose of the charge bank is lesser with calcine charging, the height of the charge pile must be lower or the width of the furnace must be greater than for the bath smelting type. A particular hazard in side charging is the possibility of a portion of the charge bank flowing, caving in, or sloughing into the molten bath and creating a rapid or even explosive reaction between charge and bath with an accompanying boiling and rapid gas evolution, particularly with regards to green or wet feed charging. When using the latter there have been rare instances where the generated pressure was strong enough to damage the furnace arch and even blow off portions or sections.

Either spring or suspended arches may be used in furnaces of either type. If width of arch is greater than twenty-eight feet, a suspended type arch must be used as hot brick strengths limit the width of sprung arches.

B.7 SMELTING CONSIDERATIONS

In past years smelter feed consisted primarily of direct smelting ores high in gangue material, generally low in copper (3 to 10%) and comparatively high in iron and sulfur. Roasting was thus desirable to help concentrate the copper by removing some of the sulfur and oxidizing some of the iron for subsequent slag formation by combination with the silicious gangue material. In more recent years flotation methods have been developed that now eliminate most of the worthless gangue materials as well as some of the excess iron and sulfur that is not combined with the copper thus furnishing a concentrated smelter feed that can directly produce a matte of desirable grade without requiring pre-roasting. Of course, if higher grade mattes are desired, this concentrate can be roasted to remove additional sulfur and produce matte grades as high as 65% copper and high grade SO_2 gas that can be utilized for production of sulfuric acid, elemental sulfur, etc.

B.7.1 CALCINE SMELTING

The grade of matte desired and the sulfur content of the smelter feed determines the need for pre-roasting, although desired production of sulfuric acid, or need for increased furnace capacity are other considerations.

The smelter feed may be calcined in flash, multi-hearth, or fluo-solid roasters. The primary objective is the elimination of the first atom of sulfur combined with the iron. Over-roasting produces sulfates and magnetite and results in a "dead" or unreactive furnace charge. Inevitably some metal sulfides are oxidized, principally the iron and part of any zinc or lead present. In ores containing arsenic and antimony, a percent of these elements are generally fumed off. Controls are more positive in the fluo-solids roaster, which accounts for its present popularity in new installations. Elements volatilized or fumed off in the roasters are often recoverable from the particulate matter collected in the flues by electrostatic precipitators or baghouses, and may thus be reclaimable. Most roaster gases contain strengths of SO_2 high enough for acid production and may run as high as 15 to 29 percent SO_2 in the fluo-solids type of furnace.

Anywhere from 11 to 16 percent of the sulfur content in calcine from the roasters is released in the reverberatory furnace in the ratio of about 97 percent in the exit gases and the balance in the furnace slag. Normal calcine-fed reverberatory exit gas contains about 0.4 to 1.0 percent SO_2 under ordinary operating conditions. Calcine-fed furnaces generally require between 2.5 to 4.0 million BTU's per ton of charge to smelt, the variance depending upon the refractoriness of the charge.

B.7.2 GREEN FEED (WET) CHARGE SMELTING

With advances made in hydrometallurgical and concentrating processes in recent years, a smelter feed with sufficiently high copper content usually can be obtained for direct smelting and thus eliminate the added expense of pre-roasting. As long as the charge does not contain an excessive amount of sulfur (preventing proper matte grade formation), no roasting is required.

B.7.3 PRODUCTS

B.7.3.1 Matte

Matte, which contains the metallic sulfides, is obtained almost simultaneously with the smelting of the charge and, containing the heavier base metals (Fe and Cu), settles in the lowest layer of the molten bath. At times, when more than 10 percent of the furnace charge consists of copper precipitates, a layer of molten copper has been known to lie beneath the matte. A matte grade of 40 to 45 percent Cu is most economical for subsequent converter treatment but older smelters have been operated with matte grades as low as 16 percent Cu. Lower matte grades are desirable when there is much secondary copper-bearing material such as reverts and scrap brass to be smelted in the converters and there is sufficient converter capacity available. Specialized smelting may produce a matte grade as high as 75 to 85 percent, which is difficult to treat in the converters.

The matte should be tapped from near the bottom of the molten bath, preferably through the sidewalls, in the area comprising the front 30 percent of the furnace length. Tapping techniques vary in different plants and have been covered by many articles written in the past. A matte temperature of around 1,000°C (1,800°F) is desirable for further treatment processes.

B.7.3.2 Slag

Slag, which contains the iron, most of the other base metals present and the gangue or worthless portion of the feed, forms when iron in the oxide form contacts silica in the near molten state. Traditional slag consists of a sesquisilicate or a fayalite-type slag in the SiO_2-FeO-Fe_2O_3 system. Copper is seldom oxidized at this stage, but if copper oxide is present, it follows the iron and the other base metals. Limestone is usually added to the charge to lower the melting point, increase the fluidity of the slag and react with alumina present to form a discardable slag wherein matte-copper entrainment is minimized. A common factor used in charge computation is the sidewall silicate degree. This is determined by the ratio of oxygen in siliceous (acid) materials in the charge to the oxygen in bases (such as FeO, CaO, Cu_2O, PbO, MnO, ZnO, MgO, BaO, K_2O_3, Na_2O, and usually Al_2O_3). Slags of these types have proven to have a relatively low melting point, are low in specific gravity, and separate easily from matte components.

Normal slags should not contain more than 0.4 percent copper but laxity of controls and improper operating techniques such as slag skim level too low, charge rate too high, poor metallurgical composition, or charge drop in location not giving uniform coverage, often results in over 1.0 percent copper content in some slags. In one large western copper plant, some previously discarded slag containing over 0.7 percent copper is being treated by flotation for further copper removal.

Generally, the higher the grade of matte produced, the higher the natural copper slag loss, within reasonable limits.

In some locations the slag is marketed to cement plants, as ballast for highways and railroads, or even as abrasive material. Slag itself does not deteriorate to any marked extent upon exposure to the atmosphere as illustrated by several dumps still in existence from abandoned smelters operated as far back as the early 1900's.

B.7.3.3 Furnace Gases

Furnace gases are not treated generally except for heat and particulate removal. In the interest of economics, the gases are invariably passed through waste heat boilers which recover in the range of 25 to 40 percent of the heat value in the fuel, as superheated steam. This steam is then used for generation of electricity and compressed air, etc. At one time in an Arizona location, nearly enough electricity was generated from waste heat steam to operate the smelter and most of the time the concentrator, mine, and a large amount of auxiliary equipment such as lighting, etc. This is not generally the case today, refer to Section B.10.

Often upward of 30,000 cubic meters (100 million cubic feet) of gas per furnace per day at temperatures in excess of 200°C (400°F) is involved. Gases are principally introduced into the atmosphere through stacks upward of 150 meters (500 feet) in height and the trend is now toward much higher stacks such as the $13 million 380-meter (1,250-foot) high stack at International Nickel in Sudbury, Ontario, and somewhat similar stacks at ASARCO's Hayden and Tacoma Smelters.

B.7.3.4 Dusts

In modern smelters, it is almost universal practice to remove up to 99.8 percent of the contained particulate matter in furnace gases by means of electrostatic precipitators. The solids thus separated from the gases are generally then added to the reverbs or converters as they contain enough copper to make this practice economical. Modern Cottrells are of the plate, rod, or wire types and are sectionalized so that one section can be isolated by means of dampers for "rapping" (dust removal from electrodes), without interfering with furnace draft requirements or allowing reintrainment of dust.

B.8 CONTROL INSTRUMENTATION

Within a relatively few years vast advances have been made in the instrumentation available to smelter operators. The following instrumentation type and controls are necessary to maximize reverberatory furnace operation from a centrally-located control room:

- Burner Control - Proper combustion should be maintained on each burner at all times. In order to achieve this, air and fuel feed rates should be automatically controlled by use of continuous recorded temperature and gas composition sampling at a few selected points in the furnace and flues. Manual overrides must be available to the operator in order to adjust for abnormal conditions.

- Draft Control - Two sets of automated dampers installed in the flues are desirable. The first would probably be a butterfly type automatically controlled for a slightly negative pressure. It would be followed by a vane-type, also automatically controlled to allow for wide variances in furnace conditions and draft that cannot be handled solely by the preceding damper. Each boiler must be equipped with a water-cooled inlet drop type flue damper to allow for complete isolation of the boiler for repairs, cleaning, etc.

- Automatic Charging Control - A variable-rate sealed charging apparatus should be installed at each charging port and the control should have variable rate-settings for each unit. In this way the feed-rate at each charge port can be set so as to be automatically controlled in accordance with the smelting rate in that location. Manual overrides must be available to the operator. Continuous charging is desirable insofar as it can be accomplished with proper maintenance of the charge banks or, in the case of deep bath smelting, an even spreading over the bath surface in the smelting zone.

- Observation - Constant observation of furnace interior is necessary for the operator to advantageously use the controls and overrides available to him. This is modernly accomplished by the use of closed-circuit television screens in front of the control operator instead of the old method of opening various observation ports in the furnace walls. Television viewing when coal is fired may be difficult because of greater flame luminosity.

- Furnace Atmosphere - Recorded gas analysis observations should be obtained at three or more locations within the furnace and outlet flues. If subsequent treatment of gases is to be practiced, a reading of the gas analysis entering the treatment unit should be chart recorded. Oxygen, carbon monoxide and sulfur dioxide are the primary constituents needed for control purposes.

- Temperatures - Temperature recording is needed for flame, arch, bath, matte, slag, boiler inlet and boiler outlet points. It is also desirable to know Cottrell inlet and outlet temperatures and occasional bottom temperatures. Additionally, temperatures of brickwork in specific areas should be available when desired to determine refractory thicknesses, developing hot-spots, etc.

- Manual Controls - Unless complete furnace operations are computer-controlled, it is sufficient to provide manual controls for placing of needed fettling material, fluxing variations or addition of other desired materials as dictated by observance of furnace interior and recorded data. Custom smelters will have greater difficulty in establishing computer control because of feed type variances.

- Bath Measurement - These measurements are needed at periodic intervals to determine proportion of matte to slag and to determine bottom elevations and bath depths. So far this is probably not automated anywhere but can periodically be done manually by use of sounding bars. The data should be recorded on the furnace log at desired intervals, usually no less than twice each shift. A computer printout is used at the Onahama Smelter in Japan.

- Many Other Controls - Many other controls are available, both automatic and manual, in addition to the principal ones listed. One recently available tool is a quick-analyzing procedural method for matte and slag wherein component analyses are available within an hour after taking the samples.

B.9 ENERGY CONSUMPTION FOR COPPER PRODUCTION

The energy consumption in domestic copper production[38] was 175 trillion Btu in 1973. Energy required to produce one pound of copper was 50,000 Btu in 1973; this included mining, beneficiating, smelting, and refining stages. The copper production could be divided into two main stages: Mining-Beneficiation, and Smelting-Refining. The data for 1973 for these two main stages is given below in Table B-1.

Table B-1. ENERGY CONSUMPTION FOR COPPER PRODUCTION

Stage	Btu Consumed (billions)	Btu per Pound of Copper	Percent of Total
Mining-Beneficiation	87,603	25,497	49.95
Smelting-Refining	87,773	23,935	50.05

These two main stages can be further divided into four stages: Mining, Beneficiation, Smelting, and Refining. The energy consumption for these four stages is given in Table B-2.

Table B-2. ENERGY CONSUMPTION BY PROCESS OPERATION

Operation	Energy Consumed Btu/lb of Copper	Percent of Total
Mining (average of underground and open pit mines)	7,560	15.29
Beneficiation (average of flotation, leaching, and precipitation)	17,937	36.29
Smelting	17,923	36.26
Refining	6,012	12.16
Grand Total	49,432	100.00

The smelting operation can be further divided into roasting, shops, and miscellaneous; reverberatory furnace; acid plant; converter; and anode casting. The energy consumption for all these operations for the year 1973 is given in Table B-3.

Table B-3. ENERGY CONSUMPTION BY EQUIPMENT USED

Equipment Used	Energy Consumed Btu/lb of Copper	Percent of Total
Roasting, shops, and miscellaneous	2,737	15.27
Reverberatory furnace	11,932	66.57
Acid plant	1,084	6.04
Converter	1,204	6.72
Anode casting	966	5.4
Grand Total	17,923	100.00

APPENDIX C

CONTINUOUS SIDE WALL CHARGING

Jan H. Reimers and Associates Limited

GENERAL

Continuous side wall charging of either green or calcine charge is one of the methods used for reverberatory furnaces. A bank of charge is built up along each wall of the furnace and the feed rate at each point along the wall adjusted to maintain a uniform bank. This has the advantage of protecting the side walls and exposing a large surface area to the flame. Smelting then is carried out at a uniform rate and the variations in the SO_2 contained in the off gas are minimized as compared to the gases from furnaces fed intermittently by such devices as Wagstaff guns or slingers.

Two examples of continuous side wall charging are at Inco's Copper Cliff smelter Figures C-1 and C-2 and Noranda's Gaspé Smelter Figures C-3 and C-4 copper smelter.

CONTINUOUS GREEN CHARGE

The Gaspé copper smelter went into production in 1955 and is described in a paper presented to the AIME in 1957.[39] This smelter was designed to treat 450 STPD of concentrate and employed green side wall charging up until 1973 when a fluid bed roaster was installed.

The initial installation is described in the 1957 paper[40] and shown in the above mentioned figures. The green charge is fed to 94.5 foot long drag conveyors located on each side of the furnace, which feed vertical charge pipes spaced at 3 ft. intervals along the furnace. Concentrates are charged for a distance of 70 feet

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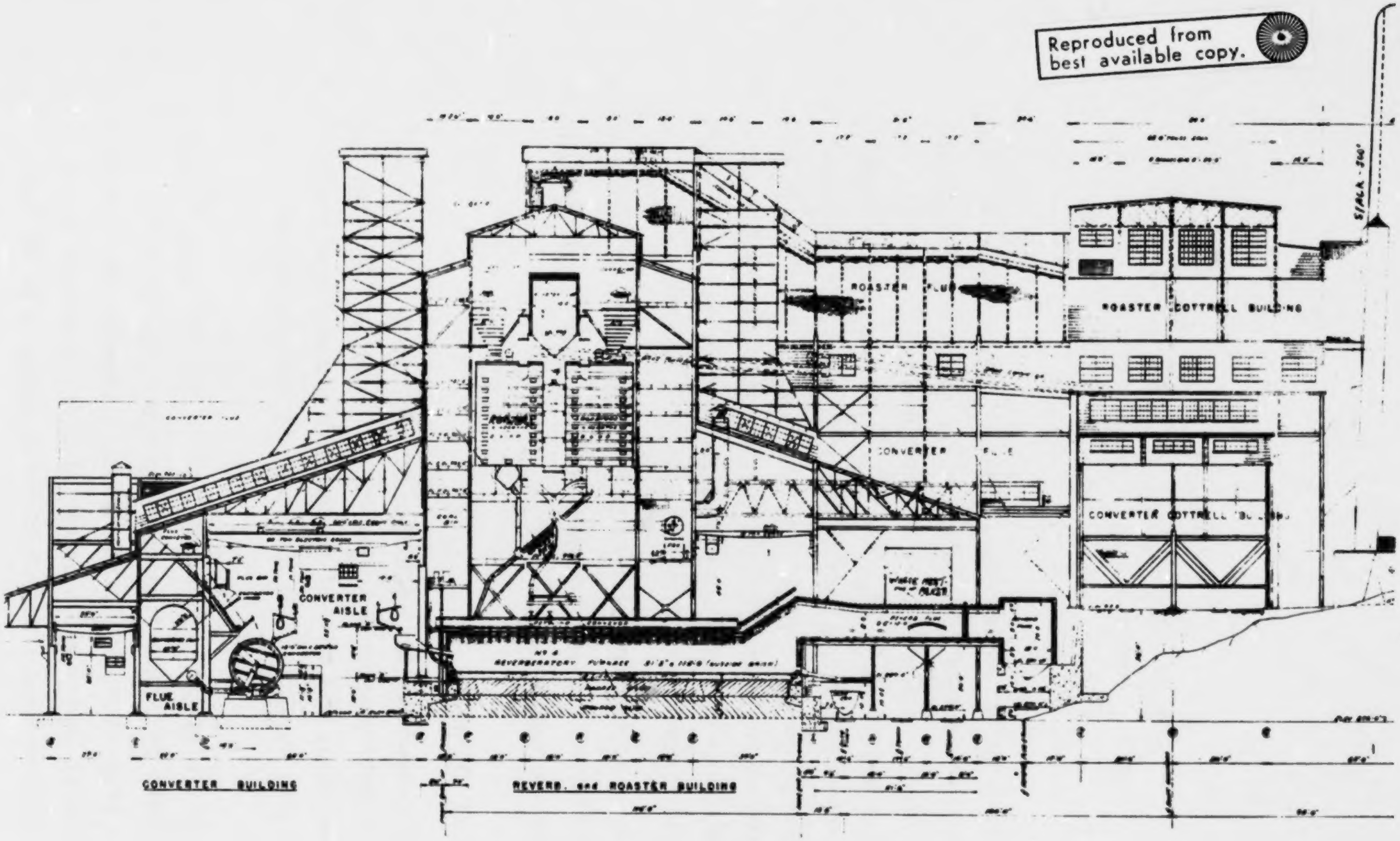
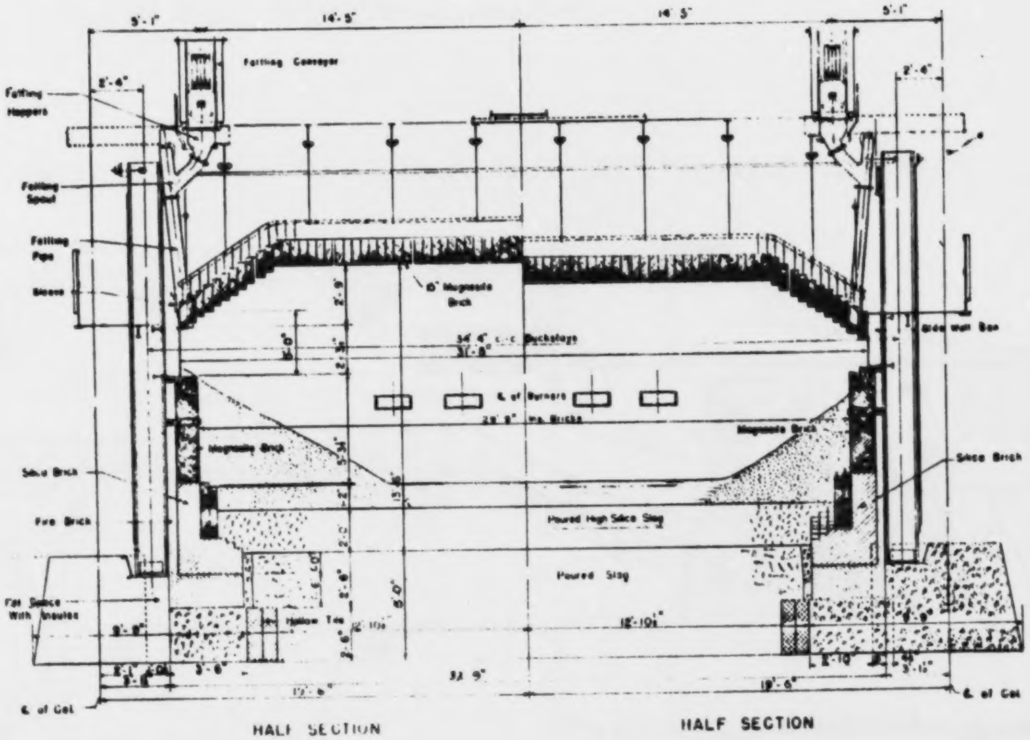

STACK - 340'
ROASTER COTTRELL BUILDING
ROASTER FLUE
CONVERTER FLUE
CONVERTER COTTRELL BUILDING
CONVERTER AISLE
FLUE AISLE
No 6 REVERBERATORY FURNACE
CONVERTER BUILDING
REVERB. and ROASTER BUILDING

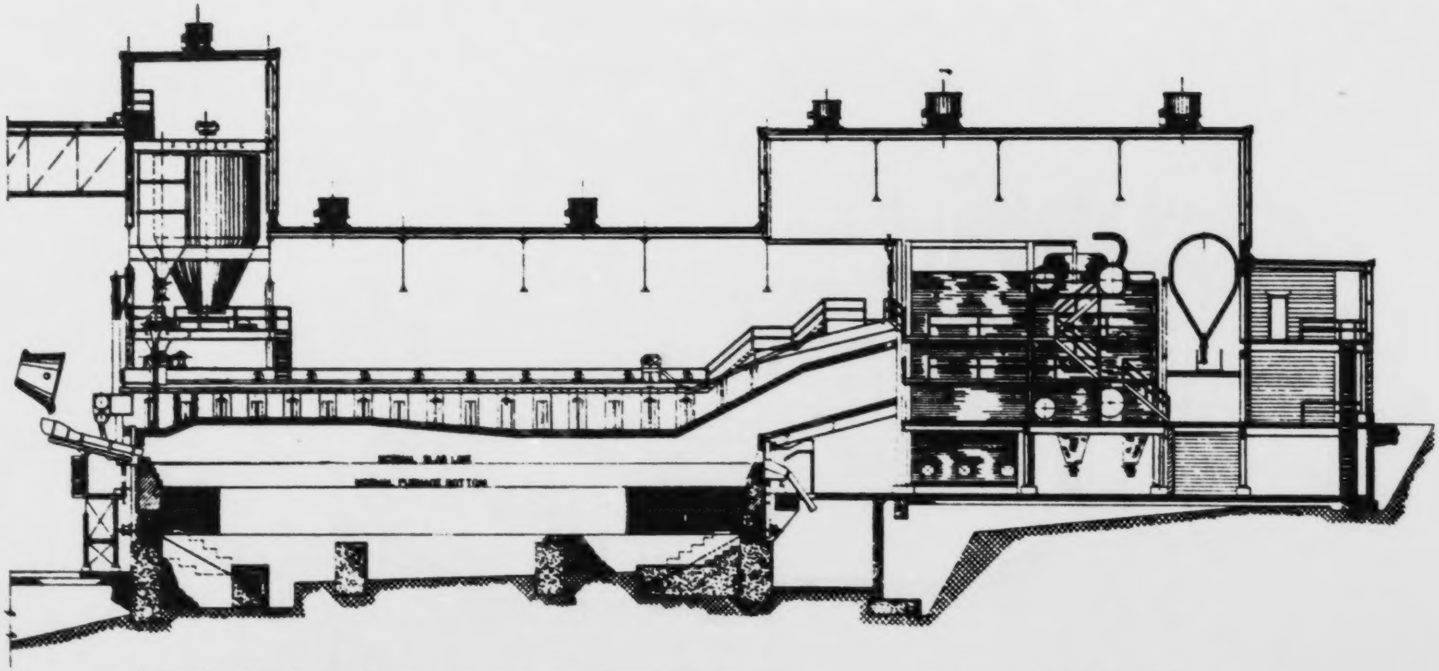
CROSS - SECTION OF SMELTER, LOOKING WEST

Figure C-1. INCO METALS LTD. - COPPER CLIFF SMELTER


5'-1"
14'-5"
14'-5"
5'-1"
Fettling Conveyor
2'-4"
2'-4"
Fettling Hoppers
Fettling Spout
Fettling Pipe
Sleeve
10" Magnesite Brick
34'-4" c-c Buckstays
31'-8"
6'-0"
℄ of Burners
28'-8" Ins. Bricks
Magnesite Brick
Magnesite Brick
Side Wall Bar
Silica Brick
Silica Brick
Fire Brick
Poured High Silica Slag
Poured Slag
Fat Space With Insulex
Hollow Tile
12'-10½"
6'-0"
32'-9"
19'-6"
19'-6"
2'-10"
3'-10"
3'-6"
℄ of Col.
℄ of Col.
HALF SECTION
HALF SECTION

INCO METALS LTD. - COPPER CLIFF SMELTER

Figure C-2. Cross Section Reverberatory Furnace



Longitudinal section through REVERBERATORY FURNACE and WASTE HEAT BOILERS

Figure C-3. Gaspe Copper Mines Smelter

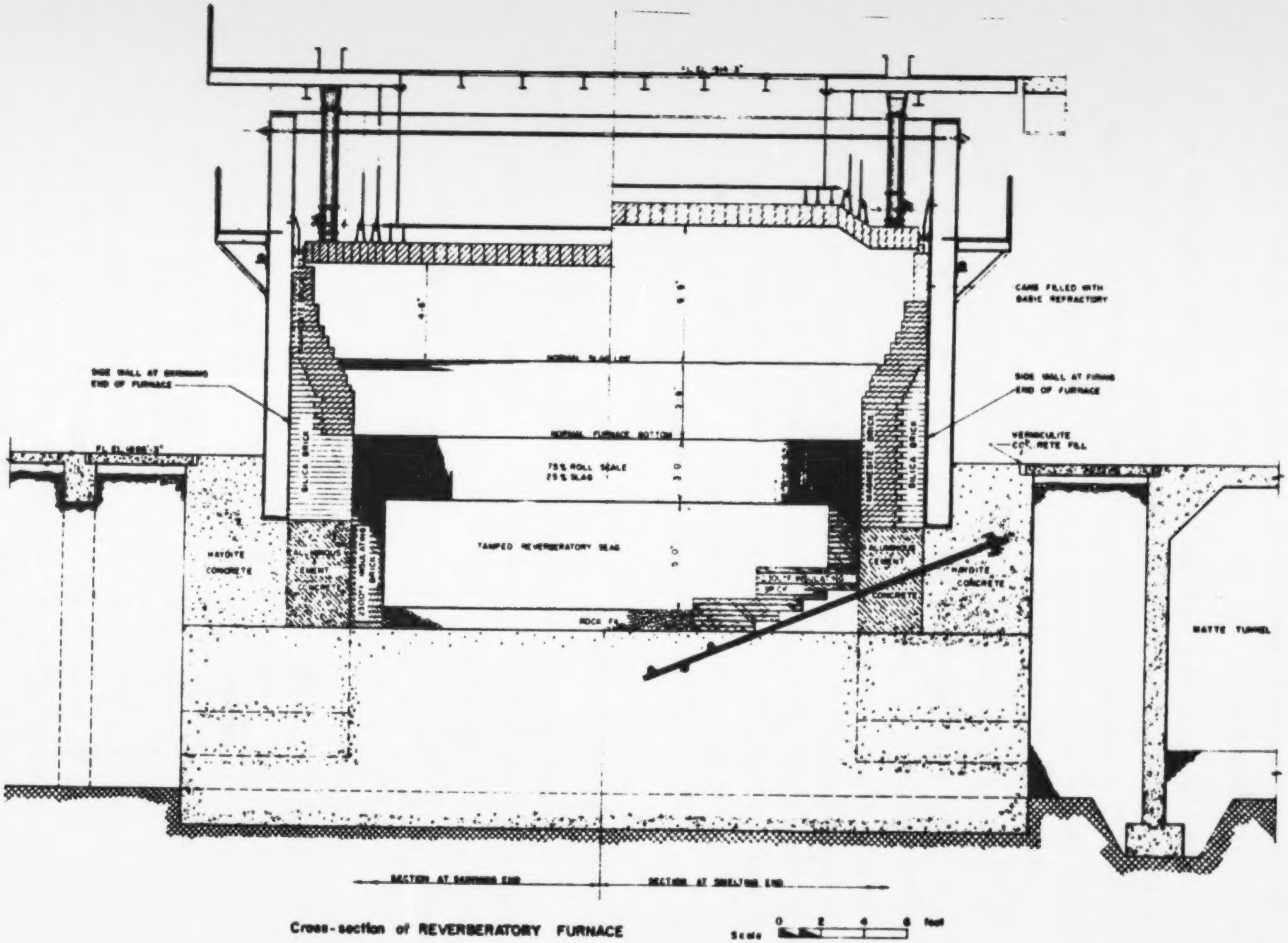

CANS FILLED WITH
BASIC REFRACTORY
SIDE WALL AT SKIMMING
END OF FURNACE
SIDE WALL AT FIRING
END OF FURNACE
VERMICULITE
CONCRETE FILL
FL. EL.
SILICA BRICK
MAGNESITE BRICK
NORMAL SLAG LINE
NORMAL FURNACE BOTTOM
75% ROLL SCALE
25% SLAG
TAMPED REVERBERATORY SLAG
ROCK FILL
2300°F INSULATING BRICK
ALUMINOUS CEMENT CONCRETE
HAYDITE CONCRETE
MATTE TUNNEL
SECTION AT SKIMMING END
SECTION AT SMELTING END
Cross-section of REVERBERATORY FURNACE
Scale
0
2
4
6
feet

Figure C-4. Gaspe Copper Mines Smelter

from the firing wall, whereas the remaining 25 feet are fettled with siliceous flux.

Shortly after start-up the drag conveyors were replaced with a belt conveyor system to reduce maintenance. With this arrangement a reversible belt was used to supply the charge pipes. The concentrate filter cake, averaging 9 to 10% moisture, was fed to the furnace at rates from 500 up to 700 STPD.

Although some operators, using green charge reverbs, have in the past experienced severe sluffing of the charge bank and puffing of SO_2, this was not the case at Gaspé. In fact, some sluffing was preferred to prevent a bench building up on the bank. The system worked well up to 1973 when a fluid bed roaster and calcine charge system was installed as part of a program to increase throughput. A similar green charge system, however, is still in use on the two reverberatory furnaces in operation at the Noranda smelter in Noranda, Quebec.

CONTINUOUS CALCINE CHARGE

The reverberatory furnaces at the Copper Cliff smelter of Inco Metals Ltd. are side wall charged with calcine on a continuous basis. This smelter has been in operation for a number of years and is described in two special issues of the Canadian Mining Journal.[41,42]

Copper-nickel concentrate and silica sand flux are partially roasted in Herreschoff roasters, located above the furnaces, to produce a calcine which is fed directly to surge bins. These feed the drag conveyors on either side of the furnace. The overall cross-section of the reverberatory building and a furnace are shown in the attached figures. Cottrell flue dust is added to the drag conveyor and the charge distributed to the drop pipes. With dry charge it is possible to use a slide gate in each pipe to control the charge distribution and maintain a uniform bank along each side of the furnace. The banks cover approximately 70 feet of the side wall, measured from the burner end.

Approximately 1500 STPD of dry solid charge is smelted in each furnace at Copper Cliff. By locating the roasters directly over the furnaces the calcine enters the furnace at approximately 1000° F and this provides some saving in furnace fuel.

Other than maintenance on the drag conveyors, no serious problems have been experienced over the years with continuous calcine charging at Copper Cliff. On the contrary, it has the advantage of enabling the operator to adjust feed distribution along the furnace and maintaining a uniform bank, through adjustments to the fettling dampers. Inspection of banks indicate no excessive puffing of SO_2 or sluffing of the charge.

SUMMARY

Continuous side wall charging is one of the practical and proven methods of charging a reverberatory furnace. It has the advantage of protecting the side walls, an important consideration if oxygen enrichment is used, and evens out variations in the SO_2 contained in the off gas. Whether green or calcine charged, there will be some inleakage of false air due to the number of feed pipe openings along the furnace. This inleakage, however, can be minimized by keeping inspection ports closed, when not in use, and by careful control of furnace draft.

APPENDIX D

RECOVERY OF COPPER CONVERTER SLAGS BY FLOTATION

A report by the U.S. Department of the Interior Bureau of Mines entitled "Recovery of Copper from Converter Slags by Flotation" by V.E. Edlund and S.J. Hussey of Salt Lake City Metallurgical Research Center in Salt Lake City, Utah discusses laboratory batch flotation tests, grindability studies, and cost studies for slag processing. This is Report of Investigations 7562 (Revised) 1972.

Laboratory batch flotation tests were conducted on copper converter slags to evaluate the relative merits of recovering copper from slow-cooled versus water-quenched slags. Three slags containing 1.6, 5.0, and 6.6 percent copper were used. More than 90 percent of the copper was recovered in a rougher concentrate leaving a 0.2 to 0.3 percent copper tailings when treating slow-cooled slag. Lower recovery and higher copper tailings ranging from 0.5 to 0.6 percent were obtained from quenched slag.

Grindability studies were made on the respective heat-treated slags. Quenched slags proved more difficult to grind than slow-cooled slags.

Cost studies showed that quenched slags can be treated at slightly lower costs than slow-cooled slags. However, the cost advantage of processing quenched slags is more than offset by the higher copper recovery obtained from slow-cooled slags.

The relative merits of treating converter slag by water-quenching versus slow-cooling indicated the following conclusions by the authors

1. Flotation of slow-cooled slag yields a higher copper recovery and a lower copper tailing.

2. Total investment and processing costs would be slightly higher for treating slow-cooled slag. These higher costs, however, would be offset by higher copper recoveries and slow-cooling would be more economical because of the additional copper recovered.

3. Quenched slags are more difficult to grind than slow-cooled slag.

4. The true economics of a method for re-treating converter slag separately would require consideration of benefits due to increased reverberatory furnace capacities, simplified furnace operations, and possible lower copper content in the reverberatory slags.

5. The amount of copper in the slag has little influence on the residual copper content of the flotation tailing.

APPENDIX E

ONAHAMA SMELTER REVERBERATORY FURNACE FLUE GAS CALCULATIONS

General Conditions[44,45]

Fuel Consumption = 6Kl/Hr = 6,000 l/Hr = 100 l/min

Sp. Gravity of Fuel Oil = 0.90 (@ 100°C)

Oil Analysis: S - 2.5%, C - 87.25%, H - 10.25%

Quantity of Sulfur Oxidized in Reverb. Bath: 3.12 T/Hr

Quantity of Combustion Components

Sulfur in Oil: $6{,}000 \times 0.9 \times 0.025 = 135$ kg/hr =
2.25 kg/min = 4.96 lb/min

Carbon in Oil: $6{,}000 \times 0.9 \times 0.8725 = 4711.5$ kg/hr =
78.53 kg/min = 173.13 lb/min

Hydrogen in Oil: $6{,}000 \times 0.9 \times 0.1025 = 553.5$ kg/hr =
9.23 kg/min = 20.35 lb/min

Sulfur in Bath: $\frac{3.12 \times 2240}{2.2046} = 3170$ kg/hr =
52.8 kg/min = 116.40 lb/min

Theoretical Air Required for Oxidation of 1 lb:

Sulfur = 4.29 lbs (1.946 kg)

Carbon = 11.53 lbs (5.23 kg)

Hydrogen = 34.34 lbs (15.58 kg)

Amount of Air Required for Oxidation

Sulfur: $(116.40 + 4.96)\ 4.29 = 520.63$ lb/min = 236.16 kg/min
= 6467.5 ft^3/min = 183.14 Nm^3/min

Carbon: $173.13 \times 11.53 = 1996.2$ lbs/min = 905.5 kg/min
= 24797.5 ft^3/min = 702.2 Nm^3/min

Hydrogen: 20.35 x 34.34 = 698.82 lbs/min = 316.98 kg/min
= 8681.0 ft^3/min = 245.82 Nm^3/min

Total Quantity of Air Required for Combustion and Sulfur Oxidation

= 183.14 = 702.2 = 245.82 = 1131.2 Nm^3/min

Quantity of Flue Gas = Air Required for Oxidation = Combustion Components

Volume of Combustion Components @ 0°C STP

$$\text{Sulfur} = \frac{116.40 + 4.96}{.089} = 1363.60 \text{ SCFM} = 38.61 \text{ Nm}^3\text{/min}$$

$$\text{Carbon} = \frac{173.13}{.0334} = 5183.53 \text{ SCFM} = 146.78 \text{ Nm}^3\text{/min}$$

$$\text{Hydrogen} = \frac{20.35}{.0056} = 3633.93 \text{ SCFM} = 102.90 \text{ Nm}^3\text{min}$$

$$\text{Wet Total} = 1131.2 + \frac{102.9}{2} = 1182.7 \text{ Nm}^3\text{/min}$$

Volume of Water = 102.9 Nm^3/min
Dry Total = 1132.7 - 102.9 = 1079.8

SO_2 Concentration

$$SO_2\text{Gas} = \frac{(116.40 + 4.96)}{.1784} \; \frac{64}{32} = 1360.54 \text{ SCFM} = 38.53 \text{ Nm}^3\text{/min}$$

$$SO_2 \text{ Concentration} = \frac{38.53}{1132.7} = 3.62\% \text{ Wet}$$

$$SO_2 \text{ Concentration} = \frac{38.53}{1079.8} = 3.57\% \text{ Dry}$$

APPENDIX F

JAPANESE REVERBERATORY FURNACE PRACTICE AFFECTING SO_2 EMISSIONS

F.1 ONAHAMA COPPER SMELTER

F.1.1 REVERBERATORY FURNACE DESCRIPTION

There are two reverberatory furnaces currently operating at the Onahama smelter in Japan. With the exception of the one reverberatory furnace at the Naoshima smelter these are the only furnaces of this type in operation in Japan. Table F-1[46] summarizes the furnace design configuration.

Typical Onahama smelter sulfur balance is shown below in Table F-2 indicating 99.7 percent sulfur eliminated from the stack gas.

F.1.2 METALLURGICAL PROCESSING TECHNIQUES INFLUENCING SO_2 EMISSIONS FROM THE ONAHAMA FURNACE

The green charge furnaces are used at Onahama as a result of a study that was made comparing this approach with a calcine charge reverberatory furnace, flash smelting furnaces, and the Mitsubishi continuous smelting process. Economy, actual results, risk factor, and technical level of the company were all considered at the time the smelter was redesigned for increased capacity. Expansion was also limited by the smelter layout and available space. Since any new smelting system would necessitate additional new preparatory systems, it was determined that the conventional green charge reverberatory furnace would be used. A bedding system is used to control charge composition. A total of 55,000 tons of concentrate are handled per month plus scrap and blister of an additional 4,000 tons per month.

Table F-1. ONAHAMA SMELTER REVERBERATORY FURNACES

	Number 1	Number 2
Fuel	Bunker C oil	Bunker C oil
Length[a]	34 m	34 m
Width[a]	10 m	11 m
Height[a] (burner side)	3.6 m	4 m
(boiler side)	3.4 m	3.4 m
Bath depth	0.8 m	1.1 m
Section area of flue	10 m^2	12.5 m^2
Number of burners	8	8
Waste heat boilers		
Number	2	2
Capacity	70% (x2)	100% (x2)
Steam generation (maximum)	32T/H (x2)	47T/H (x2)
Age	12 years	3 years

[a] Inside brickwork

Table F-2. SULFUR BALANCE FOR THE ONAHAMA SMELTER

INPUT	Tons Per Month	Percent	OUTPUT	Tons Per Month	Percent
Concentrate and ore	15,554	93.9	Acid	12,562	75.5
			Gypsum	2,721	16.4
Fuel oil	243	1.5	Slag	308	1.9
Reverts (recirculating)	793	4.6	Convert Dust	51	0.3
			Reverts (recirculating)	793	4.7
			Granulating & wash water	108	0.7
			To atmosphere	47	0.3
	16,590	100.0		16,590	100.0

It is necessary to repair and replace portions of the furnace roof every six months to minimize leakage. This is particularly true within an area of approximately 10 meters of length from the burner end.

There have been some problems with a small area in the arch at the point where the oxygen-fuel burners pass through. This resulted from the fact that this point was cooled by the burner feed line to a point where it was 150°C below the dew point resulting in corrosion. No cooling jackets are used for the ports.

The amount of 140 Nm^3 of oxygen per ton of charge was the maximum used in a test furnace. Oxygen is only used in the main furnace when an increase in capacity is required.

The following describes the sealing and oxygen enrichment techniques for increasing SO_2 concentration in the reverberatory furnace offgas at Onahama, and is taken directly from Reference 47.

"Efforts to enrich SO_2 concentration of the reverb offgas were made in two ways; one to minimize air infiltration, the other to apply oxygen to the reverberatory furnace. Air infiltration into the offgas, which had amounted to approximately 50 percent of the furnace exit gas at the uptake, was reduced to less than 15 percent by eliminating air leaks through crevices, clearances and openings of the furnace roof, side walls, fettling chutes, damper slots, expansion joints, peep holes, cleaning doors and especially dust discharging hoppers of the boilers and the Cottrell treaters. Careful and accurate draft control of the furnace also served for this purpose to a large extent.

The technique of oxygen application is different from the conventional way of using oxygen enriched air for combustion of the main burners. This technique is in some ways similar to the oxygen-fuel roof burner applied to the open hearth of steel making works. Two oxy-oil burners are installed vertically penetrating the roof of the reverb and the intense heat of the flame is directly transferred to the exposed slopes of the banked charge around the midway of the reverb, where the melting rate is low in customary operations.

Converter slag is returned to the reverberatory furnace. Approximately 49 ladles per day are returned. Each ladle contains nine cubic meters. When converter slag is returned to the reverberatory furnace the slag return door is opened, the molten slag poured in and the door closed.

There is approximately 15 to 20 percent magnetite in the converter slag. Nearly half of this is reduced in the reverberatory furnace. Therefore the converter slag does contribute to the SO_2 emissions. Some of this increase will be balanced out by dilution when air enters the slag return.

SO_2 fluctuations appear to be primarily influenced by the charging rate and frequency of charging. The chart in Figure F-1 shows output SO_2 versus time. The range generally is from 2.0 to 3.2 percent.

The use of preheated air will increase the SO_2 concentration by a small amount. Approximately 1 percent of the total sulfur input comes from the furnace fuel oil.

Pressure control is set by sensor just before the uptake which is connected to a damper downstream of the boiler. This control pressure is reset every week or so by observation of leakage out the roof. Figure F-2 shows the variation of pressure versus the length in the furnace.

Temperature is controlled and measured by optical pyrometers or Temp Stiks. The pyrometer is used at the matte tap hole and the uptake. Furnace temperature is controlled by changing the fuel rate.

Vertical stratification of SO_2 has been detected in the furnace. The maximum amount of SO_2 appears approximately one meter above the bath and decreases from this to zero at the roof.

The major leakage points in the reverberatory furnaces are at the two slag return doors, the charge ports, the burner entry (eight burners), cracks, the oxy-fuel burner ports and the bath measuring ports.

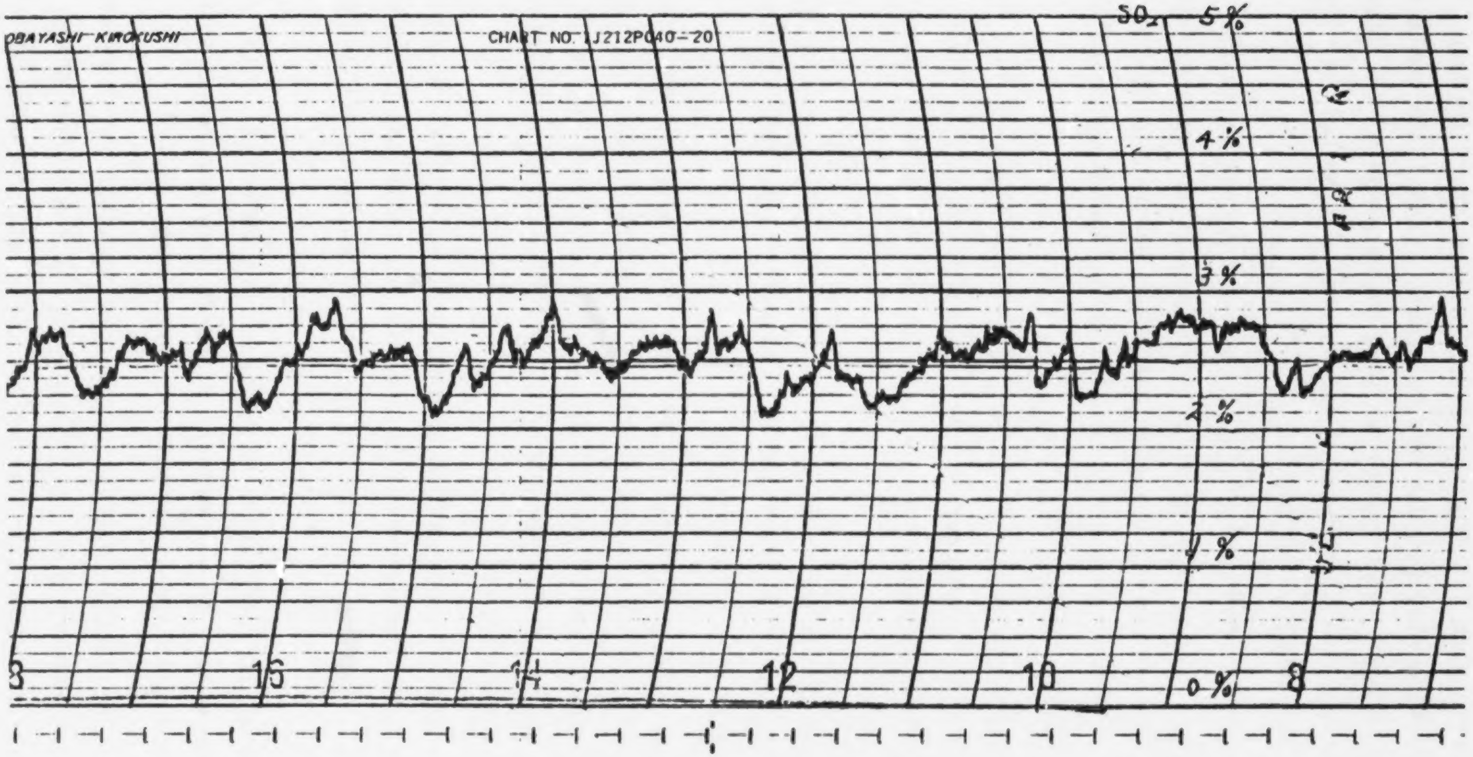


Figure F-1. PERCENT SO_2 EMISSIONS VERSUS TIME FROM ONAHAMA REVERBERATORY FURNACE

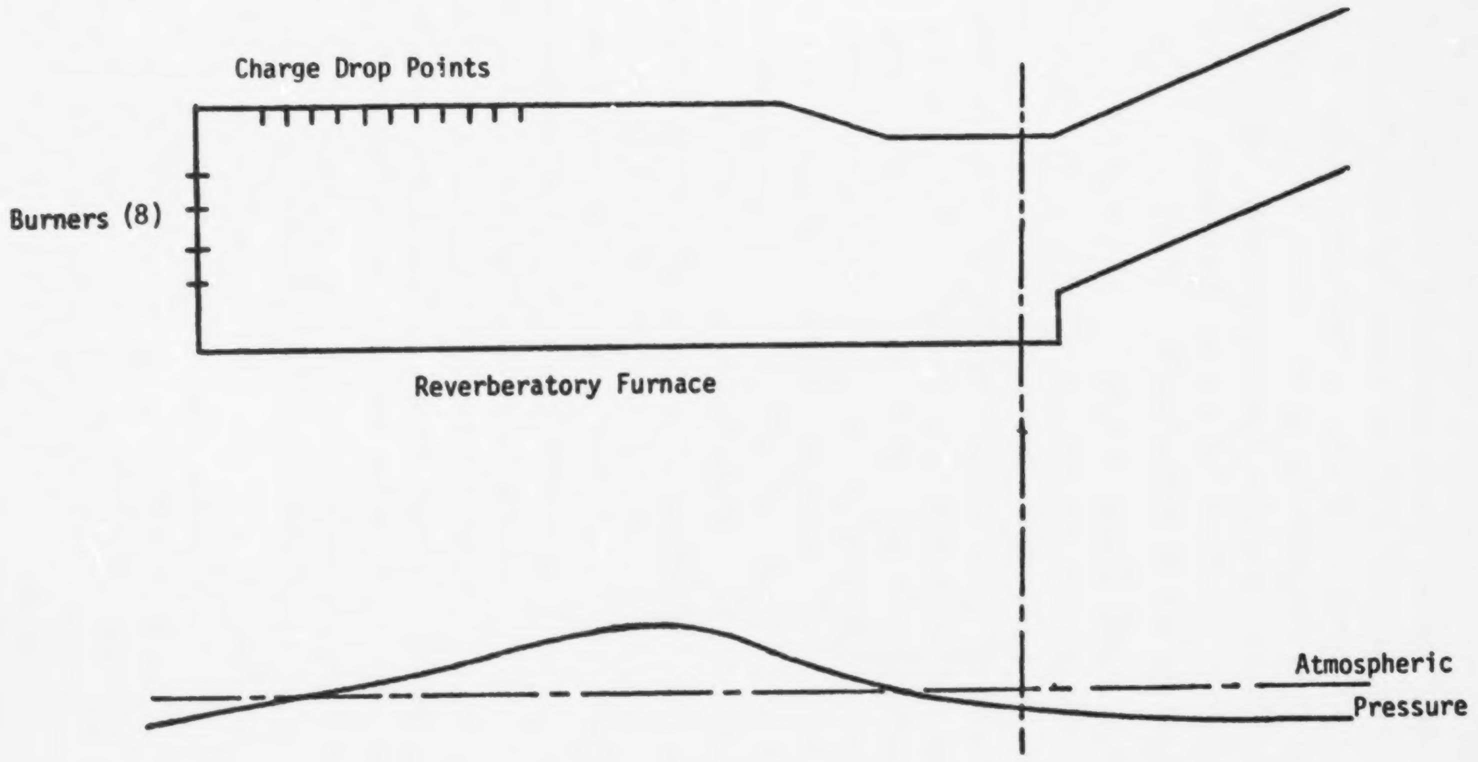

Charge Drop Points
Burners (8)
Reverberatory Furnace
Atmospheric
Pressure

Figure F-2. Pressure Variation Along Centerline of the Reverberatory Furnace at Onahama Smelter

Firing rate of individual burners, oxygen-oil ratio, shape and speed of flames, angle and position of burners and the method of furnace feed have proven to be of vital importance through three years' operation in a pilot furnace. Inappropriateness of these conditions causes increase slag loss, accretion of furnace hearth, brick damage to walls and roofs and other unusual and hazardous problems. Application of oxy-oil burners to the reverb furnace has increased by about 15 percent both smelting rate and SO_2 concentration of offgas."

"The fuel of the burners is Bunker C oil. High pressure pure oxygen atomizes and burns the fuel in the furnace upon the fettling slope. The very short high temperature flame directly melts down the charged concentrate at an extremely rapid rate. Table F-3 shows the specifications on these oxygen oil burners. Through extensive test operations over several years, it has been found that by using oxygen-oil burners, 3,000 tons of concentrate can be smelted additionally per month and the SO_2 strength in the exhaust gas can be increased by 0.3 percent per one burner. These auxiliary burners are suitable for use with green charged reverberatory furnaces to increase capacity without increasing exhaust gas volume. Therefore, theoretically, it is possible to increase the smelting capacity merely by increasing the number of burners, and finally the exhaust gas from the reverberatory furnace can be handled by contact type acid plant without any heat supply from outside. From the viewpoint of the damage to the furnace roof brick, this system is undoubtedly superior to the oxygen enrichment system for the main burners. However, still many problems remain. For example, there must be a heat balance between auxiliary burners to ensure smooth operation."

Table F-3. OXYGEN-FUEL BURNER

Fuel	Bunker C oil
Fuel consumption (max.)	0.4 m^3/Hr
Oxygen consumption (max.)	1,200 m^3/Hr
Oxygen pressure	5.0 kg/cm^2
Length	1,930 mm
Diameter	150 mm
Cooling system	Water Jacket

F.2 NAOSHIMA COPPER SMELTER

F.2.1 DESCRIPTION

The Naoshima copper smelter is located on Naoshima Island which lies in the Seto inland sea of Japan about 300 kilometers west of Osaka.[48] In addition to the conventional calcine charge (from fluid-bed roasters) reverberatory furnace, an unconventional series furnace that combines three metallurgical stages (which are normally carried out in separate furnaces) as one continuous line has been placed in operation. A detailed description of this smelter is included in Appendix G.

The furnace charge prepared in a bedding yard, using computer analysis, is conveyed to a fluid-bed roaster to be partially roasted. At least 10 different concentrates are processed at the present time with no noticeable variations in SO_2 emissions due to this factor. Flux for the reverberatory furnace is also added to improve fluid-bed operation and to heat up the material prior to furnace feed. About 40 to 45 percent of the sulfur in the charge is eliminated in the roaster. Gases from the roaster are sent to the acid plant for direct processing for SO_2 control; the principal reason why this roaster is used.

F.2.2 FACTORS AFFECTING SO_2 EMISSIONS AT THE NAOSHIMA SMELTER

The average sulfur dioxide volume percent on a dry basis from the reverberatory furnace is 1.5. Maximum SO_2 occurs approximately one minute after dropping a charge through one of the six Wagstaff guns at approximately 2.7 percent SO_2. Minimum concentration is approximately 1.0 percent. No oxygen enrichment is used at the present time. A charge is dropped at approximately every five minutes from one of the guns. The sulfur dioxide sensor is located downstream of the reverberatory furnace precipitators.

Matte averages 42 to 43 percent copper, 25 percent sulfur, and 29 percent iron. Sulfur elimination occurs at 40 percent in the roaster, 5 to 10 percent in the reverberatory furnace, and 50 to 55 percent in the converters.

Reverberatory furnace offgas composition includes 3 percent oxygen at the uptake and this is increased to approximately 5 percent oxygen at the acid plant inlet due to leakage.

Reduction of calcine magnetite by oxidizing of concentrate does tend to produce a small additional amount of sulfur dioxide in the furnace. The exact amount has not been determined.

APPENDIX G

NAOSHIMA SMELTER

Reverberatory furnace smelting of calcine from hearth roasting of copper concentrate started at Naoshima in 1918.[49,50] Both domestic and foreign concentrates are processed. A smelter addition of slightly greater capacity than the original smelter and using a fluidized bed roaster, Figure G-1, was constructed in 1969. This addition effectively added an entirely new conventional smelter including a second reverberatory furnace. Except for minor differces, the second smelter was essentially a duplicate of the old smelter with roasters, reverberatory furnace, and converters.

Development work on the new continuous Mitsubishi process (Section 8.6) began in 1961 and a prototype pilot plant was constructed and operated at the Onahama smelter. When the pilot plant operation proved the technical feasibility of the process, Mitsubishi built a semi-commercial plant at Onahama which was started up in November, 1971. The old original smelter section at Naoshima was closed in 1973 and a prototype continuous smelter of 50,000 TPY capacity was started up in 1974 in its place.

The new continuous smelting process off-gases are now combined with the presently operating (No. 2) reverberatory furnace offgases. These gases may be directed to one of three sulfuric acid plants. Roaster and converter gases are blended and passed to a double contact acid plant.

The roaster gases are passed to a cyclone dust collection system Figure G-2.

Operating data for the dust collection system is:

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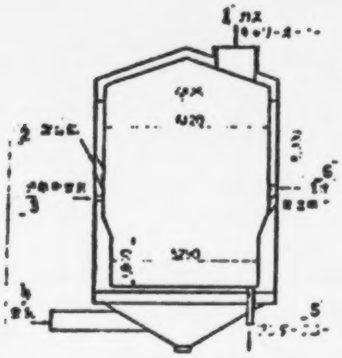

Figure G-1. Lateral View of Fluid Bed Roaster

1 -- GAS CARRIER OUTLET; 2 -- FEED PORT; 3 -- AIR FOR DISPERSION; 4 -- AIR; 5 -- MATERIAL UNDER FLOW; 6 -- WATER SPRAY

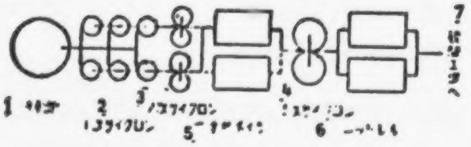

Figure G-2. Fluid Bed Roaster Gas Treatment System

1 -- FLUID FURNACE; 2, 3, and 4 -- PRIMARY, SECONDARY, AND TERTIARY CYCLONE; 5 -- PREHEAT BOILER; 6 -- COTTRELL; 7 -- TO SULFURIC ACID TREATMENT

- Primary cyclone efficiency - 90 percent
- Secondary cyclone efficiency - 70 percent
- Steam generated by roaster waste heat boilers - 7.5 tons per hour
- Electrostatic precipitator efficiency - 99.6 percent.

The following shows typical operating data for the fluosolids roaster:

- Roaster Charge - 53 wet tons per hour
- Blown in air - 300 Nm^3/min (10,593 SCFM)
- Bed space velocity - 80 cm per second
- Tuyere pressure drop - 780 mm water
- Bed pressure drop - 1,500 mm water
- Bed temperature - 630°C
- Freeboard temperature - 560°C
- Freeboard draft - ± 0 mm water
- Exit gas to acid plant
    - Volume 530 Nm^3 (18,715 SCFM)
    - SO_2 concentration - 11 percent
    - Temperature - 300°C
    - Dust content - .0047 gr/scf
- Thermal Output
    - Gas heat content - 57 percent
    - Calcine heat content - 38 percent
    - Other losses - 5 percent

G.1 REVERBERATORY FURNACE

The partially roasted calcine is conveyed by chain conveyor from the roaster to the calcine hoppers above the reverberatory furnace, Figure G-3. The calcine is then charged into the furnace through the side wall by Wagstaff guns with direct television viewing of the bath by the operator. These Wagstaff guns are arranged in such a way as to allow an even distribution of the calcine over the bath in the furnace. The furnace is fired with Bunker C oil through six low pressure burners.

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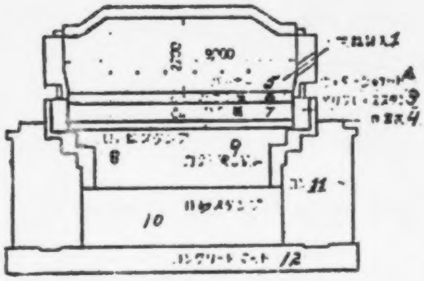


Figure G-3a. Vertical Cross Section of Reverberatory Furnace:

1) ORE CHARGE; 2) WATER JACKET; 3) CLAY LAYER; 4) OPERATIONAL PLATFORM; 5) BURNER; 6) SLAG LAYER; 7) MATTE LAYER; 8) CHROME ORE LAYER; 9) CAST SLAG; 10) SAND LAYER; 11) CONCRETE; 12) CONCRETE MAT

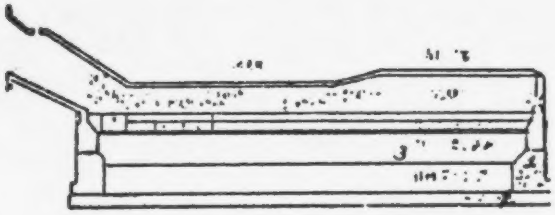


Figure D-3b. Lateral View of Reverberatory Furnace

1) CONCRETE;
2) CONCRETE MAT;
3) SAND LAYER;
4) REMAINDER ILLEGIBLE

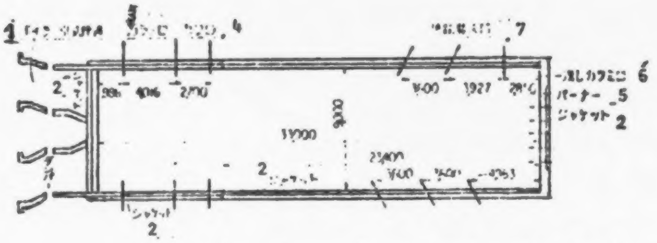


Figure G-3c. Reverberatory Furnace Overhead View

1) OFFGAS DUCT TO BOILER-NEGATIVE PRESSURE; 2) JACKET; 3) SLAG OPENING; 4) MATTE OPENING; 5) BURNER; 6) RETURN SLAG OPENING; 7) WAGSTAFF GUN FOR CHARGING FURNACE

Figure G-3. Structural Views of Naoshima Reverberatory Furnace

Matte averaging 42 to 43 percent copper, 25 percent sulfur, and 29 percent iron, is tapped from any of four tap holes, located two on each side, and transported to the converter aisle by electrically operated cars. Slag is skimmed from the skimming hole near the uptake end of the furnace, is granulated by seawater, and conveyed to the slag stockyard. The gas from the furnace is cooled in waste heat boilers and treated by the electrostatic precipitator which reduces the dust content to less than 0.003 gr/scf.

Specifications for the reverberatory furnace are as follows:

- Length - 33 m
- Width - 9 m
- Height - 3.76 m
- Smelting capacity - 8,000 tons/month
- Bunker C fuel consumption - 100 liters per ton solid charge
- Steam generated in waste heat boiler - 33 tons per hour
- Precipitator collection efficiency - 98 percent

The structural characteristics of this bath-type furnace are described as follows:

1. The floor of the reverberatory furnace is composed of solute slag 2.3 meters thick above a 2-meter thick layer of sand set on the inner surface of concrete constructed above rock.

2. To prevent seepage of matte downwards, chrome ore and magnetite layers are above this. Thus, an imprevious furnace floor is produced.

3. The shape of the bath portion is that of a crucible. To prevent erosion of the furnace wall near the slag line, a water-cooled jacket of cast copper section 510 mm high is extended along the entire slag line.

4. The crucible wall is made of clay. The settling zone wall, the burner wall and the vertical wall are lined on the inside with chrome-magnesite brick (magnesia-bricks near the matte and slag apertures), while the outside is chrome-magnesite brick. The ceiling is a suspended structure of chrome-magnesite brick. A portion of the ceiling panel can be adjusted to control its temperature.

5. The path for the gases to the boiler is inclined at an angle of 26°, and is made as broad and as short as possible to prevent blockage from accidentally occuring.
6. In order to improve the thermal efficiency and the draft, the ceiling at the burner end is raised.
7. There is a slag return opening in the roof above the burner. This opening is normally closed and not used.

The walls and roof of the furnace appeared to be very tightly sealed.[51] The roof had gaps between the bricks at the outer surface but were sealed at the inner hot-side. The outer gaps are presented to allow expansion and contraction of the bricks within the reverb arch. On walking around the roof there were a few areas where gas could be detected but, in general, most of the area was free of noticable odors.

The point at which the burners enter the burner wall is tightly sealed and there are not other openings. There are some points where a charge could be dropped through the roof, however, these are closed by dampers.

Oxygen enrichment has not been used in this furnace. They do have an oxygen plant at the smelter and do have the capability of using it if desired. They also have the capability of using preheated air. What is used depends upon specific smelting problems they have, primarily related to the production rate.

G.2 REVERBERATORY FURNACE WASTE HEAT BOILER

Because the exhaust gas of the reverberatory furnace is at the high temperature of 1,250°C, thermal recovery is carried out in a waste heat boiler, and cooling to 350°C results. Two boilers in parallel operation are usually provided, and they are designed so that one can maintain the average operational output of the reverberatory furnace when one is shut down for inspection at regular intervals. Table G-1 illustrates the characteristics of the waste heat boiler.

Table G-1. REVERBERATORY FURNACE WASTE HEAT BOILER CHARACTERISTICS

Item	Units	Design Figures
Inlet gas amount	Nm^3/min	1,030
Inlet gas temperature	°C	1,250
Outlet gas temperature	°C	350 ± 30
Supplied water temperature	°C	120
Amount of vapor generated	t/h	33
Vapor pressure	kg/cm G	40
Vapor temperature	°C	420
Steam uses	--	Electricity generation

The gas is cooled in the boiler and undergoes 90.6 percent dust removal through two sets of four horizontal Cottrells.

G.2.1 REVERBERATORY FURNACE

The objectives of the reverberatury furnace feeding system include preventing as much as possible the temperature decline of the calcine emitted from the fluo-solids roaster, the maintenance of low fuel consumption of the reverberatory furnace and the preservation of dispersibility and fluidity of calcine. To minimize calcine heat loss and facilitate handling the roaster is placed as close as possible to the reverberatory furnace.

On each side of the reverberatory furnace, there are three calcine weighing hoppers and the Wagstaff gun is located below. Upon calcine charging, the charging window of the reverberatory furnace is automatically opened, the gun is moved pneumatically into the furnace and the calcine hopper is opened. High temperature calcine is instantly distributed in a wide area, and it is rapidly smelted. High efficiency decomposition is carried out with little dust dispersion.

A television camera is used to observe the molten bath within the reverberatory furnace. When is appears that the last charge material has been melted in a given area, a new charge is introduced through the nearest Wagstaff gun. The gun position is selected by the operator. The frequency of charges is approximately once every five minutes from one gun. Each charge through the gun at 5 to 6 tons is weighed and recorded. The black and white television picture is very clear in determining when the last charge had been melted by observation of dark points and bubbles. The next charge is introduced by simply pressing a button, with everything automatic. It is a very smooth operation.

The oil buners are fitted with six low pressure jets. Further, there are two silicated ore gun feeders above the burner walls, allowing the slag composition to be controlled depending on furnace conditions.

Generally, a minus 1 millimeter of water pressure in the uptake of the reverberatory furnace is maintained. Observation of the chart during operation indicated a variation of approximately ±0.2 millimeters of water. The damper pressure control for the furnace is located at the inlet of the Cottrell. There are also manually water-cooled drop dampers at the inlet to the waste heat boilers to allow isolation for maintenance work.

There are two matte extraction outlets in both walls 24 m and 27 m away from the burner walls, the individual slag extraction outlets are similarly placed in positions 31 meters away. In usual operations, the depths of the matte and slag layers are held at 660 mm and 400 mm, respectively.

The slag is granulated by pouring into a large stream of water directly at the launder exit.

Once or twice every month a maintenance operation is conducted to replace damaged brick work. The bricks in the roof are hung by pairs with two bricks per hanger. Some arch sections are panelized. Maintenance is probably considerably more extensive than in the U.S.

G.3 GAS EMISSIONS PROCESSING

The average sulfur dioxide volume percent on a dry basis from the reverberatory furnace is 1.5. Maximum SO_2 occurs approximately 1 minute after dropping a charge through one of the six Wagstaff guns at approximately 2.7 percent SO_2. Minimum concentraction is approximately 1.0 percent. No oxygen enrichment is used at the present time. A charge is dropped at approximately every 5 minutes from one of the guns. The sulfur dioxide sensor is located downstream of the reverberatory furnace precipitators.

Matte averages 42-43 percent copper, 25 percent sulfur, and 29 percent iron. Sulfur elimination occurs at 40 percent in the roaster, 5-10 percent in the reverberatory furnace and 50-55 percent in the converters.

Reverberatory furnace offgas composition includes three percent oxygen at the uptake and this is increased to approximately 5 percent oxygen at the acid plant inlet due to leakage.

Reduction of magnetite by oxidizing concentrate does tend to produce an additional amount of sulfur dioxide in the furnace. The exact amount has not been determined.

Cleaned and blended gases from the continuous and reverberatory furnaces are treated in one of three sulfuric acid plants as determined by the operator. There are two single contact and one double contact acid plants producing 40,000 tons/month of acid which is shipped by boat to as far away as Australia.

A part of the manufactured acid (5,000 tons/month) at about 50 percent strength is bled from the drying tower and reacted with the limestone milk in reactors to make wall board grade gypsum. Three milimeter maximum size limestone is milled in a ballmill and minus 200 mesh limestone milk is prepared. The gypsum formed is separated by centrifuge.

The lime scrubber could be described as a type of Venturi scrubber, however, the water is injected at the top along the centerline of the Venturi and the gas is injected at right angles to the centerline. Sea water is now used but this will be changed in the future. No sludge occurs within this system because the liquid is maintained at below saturation (calcium sulfate) condition.

Total gypsum manufacture is 10,000 tons per month. About 2,000 tons per month of fuming grade acid (oleum) is also produced. About 98 percent of the smelter feed sulfur is fixed in slag or captured in gypsum and acid.

The Lurgi double contact acid plant produces 98-99 percent sulfuric acid. All of the exit gases from the converters and fluosolids roaster are treated in this plant. The plant consists of three semi-venturi scrubbing towers, eight electrostatic mist precipitators, ten gas coolers, a drying tower, a converter with heat exchangers and two absorbing towers.

To meet fluctuations of gas volume and SO_2 concentration, the acid plants are equipped with closed circuit TV sets, telephone and light signals so that the operator can always keep track of smelter operations.

APPENDIX H

CONVERTER PROGRAMMING

The converter programming used for this study was based on a typical converting process as utilized at the Ilo Smelter in Peru and discussed by Reference 52. This smelter uses three Peirce-Smith converters plus maintains one on reserve.

The typical converter charge consists of sixteen ladles of matte added in a 5-2-2-2-2-2-1 sequence; a ladle contains approximately 16.6 tons of matte (32- to 33-percent Cu at Ilo). The first 82.5 tons of matte (5 ladles) are added to a converter containing 5.9 tons of flux remaining from the previous charge. This flux had been used to cool the bath surface and to get a clean blister copper pour. Blowing is commenced (416.5 SCFM average). The bath temperature, initially at 2,012°F, rises until it reaches 2,147°F, at this point more flux is added, aiming at a slag assay of 24 percent silica (SiO_2).

The blowing continues until the temperature reaches 2,300° to 2,372°F. The first slag skim is made. At this point, there is still some iron sulfide remaining in the matte to impede excessive magnetite formation.

The second slag blow begins with the addition of 33 tons of matte and more flux (at temperature of 2147^{0}F). Again some of the iron sulfide is retained in the matte. The slag skim is made. The converter is skimmed 6 to 7 times and only in the last slag blow is all the iron sulfide removed.

After the slag blows are completed the copper blow begins. Scrap copper and reject blister bars are added for temperature control. When this blow is completed, a boat of flux (5.4 tons) is added and the copper is poured. The air flow is about 450.1 SCFM during the copper blow. The product is approximately 84.7 tons of copper.

The time required for this process is 11 hours and 10 minutes per charge, including 6 hours and 10 minutes for slag blowing, one hour and 50 minutes for copper blow, and 3 hours and 10 minutes of down time. This means blow time is 72 percent of the time required per charging cycle.

This is considered to represent a typical converter operation as used in the copper industry. Based on this, a basic model for estimating the SO_2 concentration and offgas volumes for converter programming was proposed. The following is a direct quote describing the model used for programming:

"The basic model for estimation of the SO_2 concentration of the converter exit gas has been derived by considering the applicable thermodynamics, as given primarily in references [53-58].

The nine chemical reactions shown in the Introduction form the proposed model. Based on the data presented by Schuhmann [53] and Ruddle [54], the partial pressure of oxygen does not appear ample to form appreciable amounts of Cu_2O during the slag blows; therefore, equation (6) shall be neglected. This was justified further by Reference [55]. The slag blow is then described by the following equations:

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2 + 223{,}880 \text{ Cal}$$

$$6FeO + O_2 \longrightarrow 2Fe_3O_4 + 151{,}800 \text{ Cal}$$

$$2FeO + SiO_2 \longrightarrow (2FeO) \cdot SiO_2 + 22{,}200 \text{ Cal}$$

$$FeS + 3Fe_3O_4 + 5SiO_2 \longrightarrow 5[(FeO)_2 \cdot SiO_2] + SO_2 + 4{,}760 \text{ Cal}$$

By the same token, if caution is exercised not to overblow the white metal-to-blister copper transition, relatively small amounts of Cu_2O will form in the blister copper, and the copper blow is described by:

$$Cu_2S + O_2 \longrightarrow 2Cu + SO_2 + 183{,}600 \text{ Cal}$$

The following assumptions are made:

1. O_2 efficiency will be taken as 75 percent, defined as

   $$\frac{\text{kg } O_2 \text{ consumed}}{\text{kg } O_2 \text{ blown}} .$$

2. Charging sequence used at Ilo will be followed. Ilo typically begins with six tons of flux used in the previous charge for cooling the bath surface and getting a clean copper pour.
3. The iron (Fe) in the matte shall be assumed to go to 80 percent FeO and 20 percent Fe_3O_4 in the slag.
4. Copper slag losses typically run from 3-5 percent, but these shall be ignored because of insufficient data on loss mechanisms.
5. A matte composition (weight, %) is assumed to be 35 percent Cu, 27 percent S, 32 percent Fe, 5 percent Fe_3O_4, and 1 percent impurities (As, Bi, Pb, Sb, Se, Te).
6. The final Fe_3O_4 level in the slag approaches 25 percent (including the 5 percent from the matte). This tacitly assumes that the reduction of Fe_3O_4 by FeS is equal to its production by oxidation of FeO.
7. The silica content of the slag is assumed to be 24-27 percent.
8. Following the work of Korakas[59], the (wt % Fe)/(wt % Cu) in the matte will be 0.025 when all the slag blows are stopped (except final blow which removes all iron from matte). This means that approximately 1 percent of Fe will remain until this final slag blow.
9. Impurities will be ignored quantitatively.

Using these assumptions and keeping the 5-2-2-2-2-2-1 sequence presented above in mind, calculations can be made using the model.

Materials/charge:

$$\text{Total charge} = 16 \text{ ladles} \times 15.091 \frac{\text{ton}}{\text{ladle}}$$

= 241,456 kg/charge

Total Cu/charge = (241,456) x (0.35) = 84,509 kg/charge

Total Fe/charge = (241,456) x (0.32) = 77,265 kg/charge

Total S/charge = (241,456) x (0.27) = 65,193 kg/charge

Total Impurity/charge = 2,415 kg/charge

Consider now the first slag blow. This blow processes 5/16 of the charge or

5/16 x 241,456 kg - 75,455 kg

Cu = 26,409 kg

Fe = 241,456 kg

S = 20,373 kg

Fe_3O_4 = 3,773 kg

Impurities = 775 kg

Remembering that the blow will be stopped when $\frac{\text{wt \% Fe (matte)}}{\text{wt \% Cu}}$ = 0.025, 23,485.2 kg of Fe will be converted to FeO and Fe_3O_4 in the ratio of 80 percent to 20 percent respectively, and 13,483.8 kg of S will be converted to SO_2. This leaves 660.2 kg Fe and 6,988.8 kg S in the matte. Therefore, 18,788 kg of Fe are used to produce FeO, and 4,597 kg are used to produce Fe_3O_4. From this it can be seen that the slag contains 24,172 kg of FeO and 6,491 kg of Fe_3O_4 plus the 3,773 kg which was in the matte originally, for a total of 10,264 kg of Fe_3O_4. The flux remaining in the converter from the previous copper pour is 5,455 kg (66 percent SiO_2), yielding 3,600 kg of SiO_2. In order to produce a slag of 25 percent SiO_2 additional flux must be added.

$$\frac{.66\,x}{(24{,}171.7 + 10{,}264) + x} = 0.25$$

x = 20,997 kg flux

20,997 - 3,600 = 17,397 kg flux

The first slag skim will remove approximately the following amount of material:

34,436	($FeO + Fe_3O_4$)
20,997	(flux)
55,433	kg (material removed)

Total oxygen requirement will equal the oxygen which combines with Fe to form FeO and Fe_3O_4 and S to form SO_2 divided by the efficiency, as follows:

5,391	kg (from FeO formation)
1,794	kg (from Fe_3O_4 formation)
13,484	kg (from SO_2 formation)
20,669	kg

$$\text{Total } O_2 \text{ required} = \frac{20,669}{0.75} = 27,559$$

Air is blown during the slag blows at 707.9 SCMM (25,000 SCF) or 148.7 SCMM (5,250 SCFM) of oxygen. This is equal to 212.3 kg/min. Therefore, it is seen that using air 27,559 kg/212.3 kg/min = 130 minutes are required for the first slag blow. The SO_2 concentration of offgases can be determined in the following manner. The average S consumption during the 130 minute blow period is:

13,484 kg/130 min = 103.7 kg/min

This S produces about 207.2 kg/min (72.5 SCMM) of SO_2 on the average. The exit stream is, then:

559.3	SCMM N_2
37.3	SCMM O_2
72.5	SCMM SO_2
669.1	SCMM Total

This produces average SO_2 concentrations on the order of 10.8 percent, or, with 100 percent dilution, 5.4 percent.

Consider now the copper blow. Neglecting the addition of concentrates and scrap copper used for temperature control, the converter contains only the white metal (all iron removed on last slag blow). The slag has been skimmed.

Material in Converter:

84,509 kg CU
21,322 kg S

Material Converted:

21,322 kg S

Oxygen Required:

$(21,322 \times 32)/(32.064 \times 0.75) = 28,372$ kg of O_2

Blow Time Using 40% O_2:

$28,372/437 = 65$ min

Rate S Consumption:

40% O_2: $\frac{21,322}{65} = 328.1$ kg/min

SO_2 Production:

40% O_2: 655.6 kg/min = 229.4 SCMM

SO_2 Concentrations (No Infiltration):

40% O_2: 28.1%

SO_2 Concentration (with 100% Infiltration):

40% O_2: 14.4% "

Scheduling of multiple converters has been examined. The SO_2 vs time for a single converter is shown in Figure H-1 using the assumptions of the simple model presented. Based on the

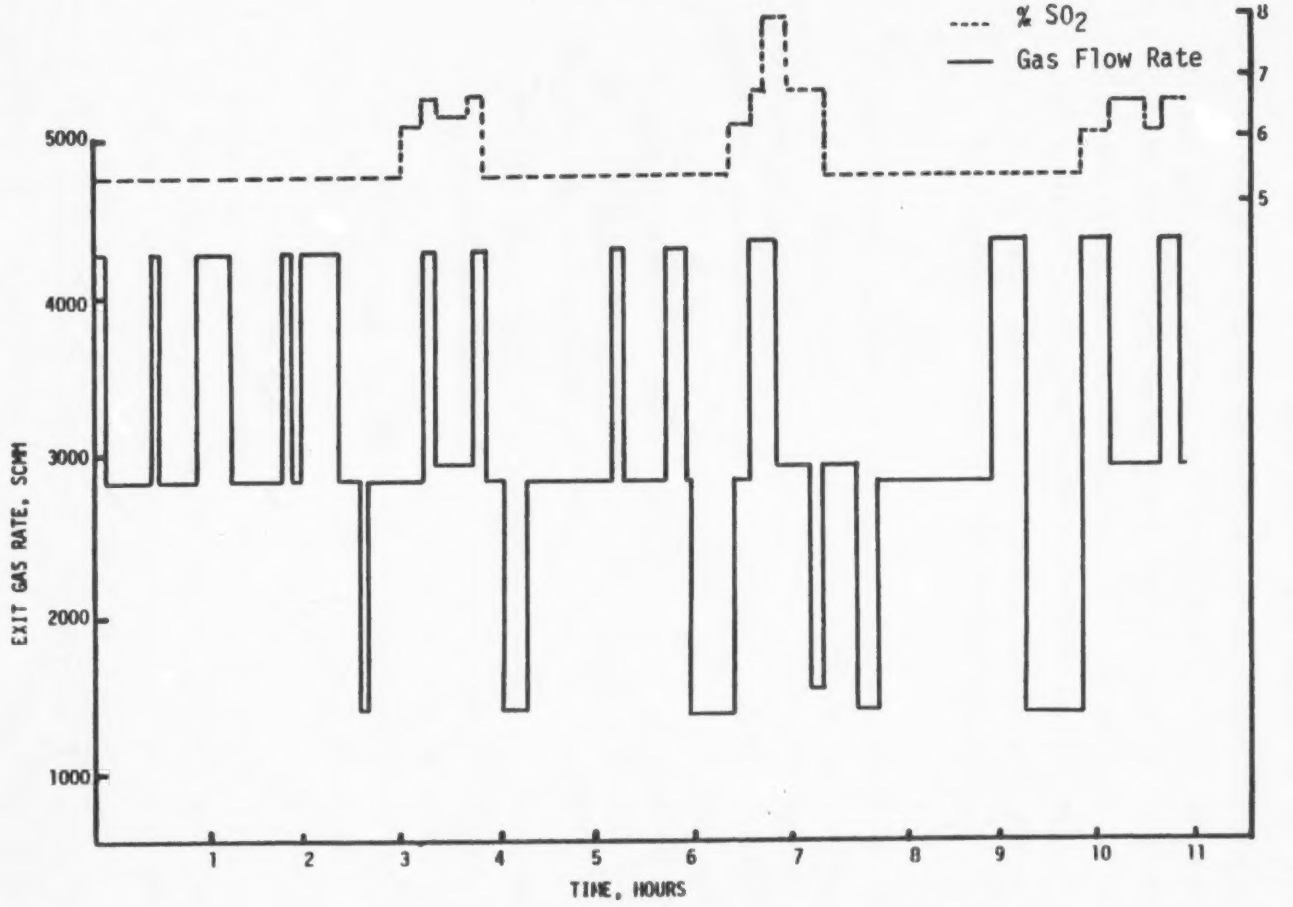


Figure H-1. Exit Gas Rate (After 100% Dilution) and SO_2 Concentration for Scheduling Scheme of Figure 2.

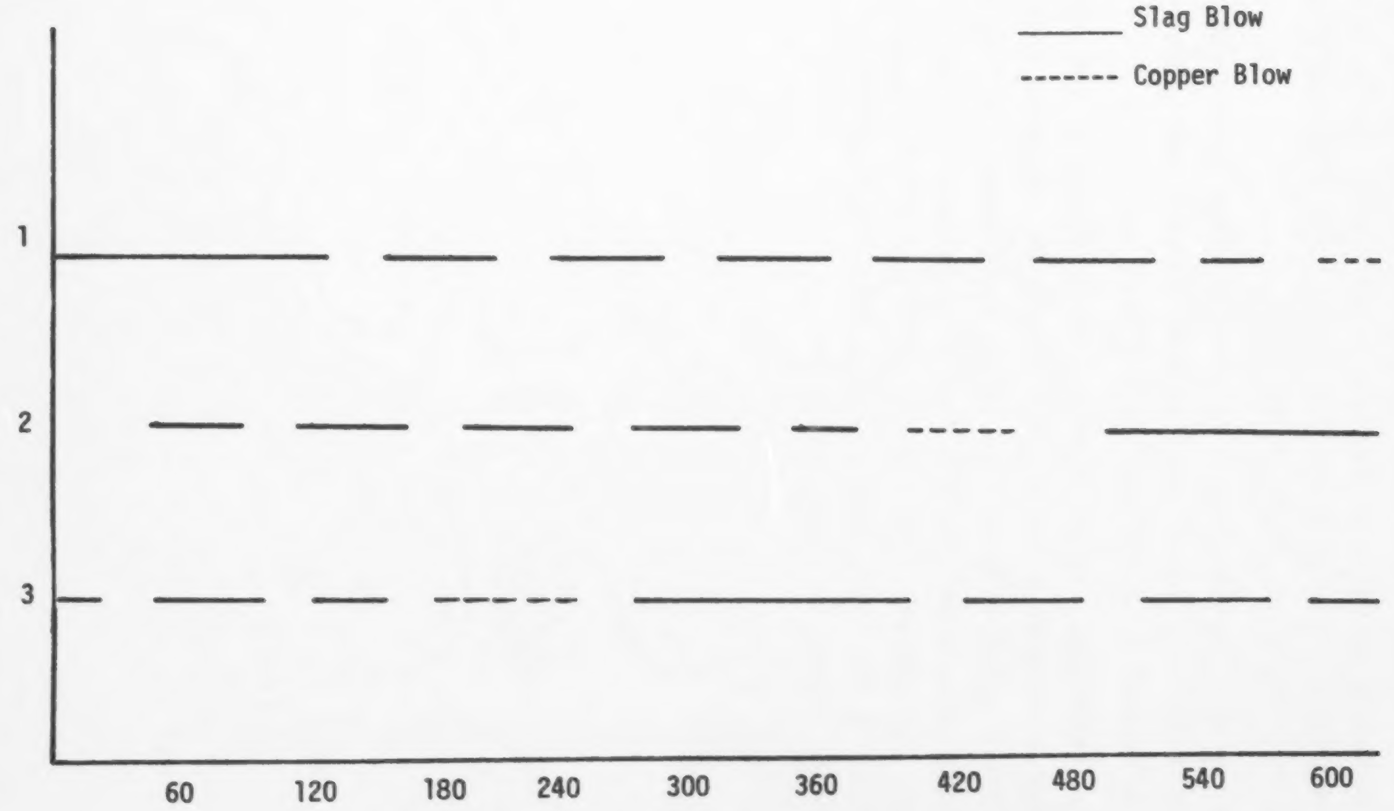
calculations, five converters would be necessary to have one converter in the copper blow at all times.

Figure H-2 shows the scheduling for three converters and Figure H-1 is an indication of the percent SO_2 at the outlet by joining the offgases of the three converters. Figure H-1 also shows the flow rate fluctuations during the operations. These figures reflect conditions after 100 percent infiltration. Based on the figure, exit gas flow rate varies from 1,416 to 4,361 SCMM; SO_2 concentration (vol percent dry) varies from 5.4 to 7.8."

Using the above model as a guide, a converter program was carried out based on the blowing times as given above. The converter program thus used in this study is presented in Figure H-2. Initially SO_2 concentrations of 7.8 and 5.4 percent were used for the copper and slag blows, respectively, as used in the basic model. Similarly volumes of 52,000 and 50,000 SCFM were used for the copper and slag blows, respectively. The resulting gas characteristics versus time were similar to those obtained by the model.

The values originally obtained for the base smelter system, Appendix Y-1, proposed converter offgas averaging 5.7 percent SO_2 at 64,500 SCFM for the smelter system under consideration. This implied each converter produced an offgas of approximately 30,000 SCFM. Also, the average gas characteristics are maintained from a sulfur balance based on 1,400 TPD concentrate.

For this study, gas characteristics between the two values are used. Thus 40,000 SCFM for the slag blow and 42,000 SCFM for the copper blow are considered representative for converter offgases. Since there are three converters, the average number blowing at any one time is two. Therefore, 82,000 SCFM is used as the average converter offgas volume. A sulfur balance indicates that 4.5 percent SO_2 at 82,000 SCFM corresponds well with the 5.7 percent SO_2 at 64,500 SCFM. Finally, the SO_2 concentrations were adjusted to give the average SO_2 concentration of 4.5 percent.



Basis: 25,000 SCFM for Slag Blow; 27,000 SCFM for Cu Blow, OSCFM for Down Time

Figure H-2. Converter Programming - 3 Converters

The actual values used in this study are shown in Figure H-3 and H-4 while numerical values are presented in Table H-1. As can be seen, the SO_2 concentration varies from 4.0 to 6.6 percent while the flow rates vary from 40,000 to 122,000 SCFM.

These values appear to be more representative of current operating practice corresponding to data reported from actual copper converters using efficient hooding and offgas systems.

This adjusted model seems feasible even for processed ores containing high impurity levels of As, Sb, Pb, and Zn. Assuming that there are still traces of these impurities in the matte, the longer slag blowing times are around 1,200°C will insure removal prior to the blister forming blow. Thus, oxygen enrichment for the copper blow should not affect the final copper quality since these impurities will be removed during the slag blows.

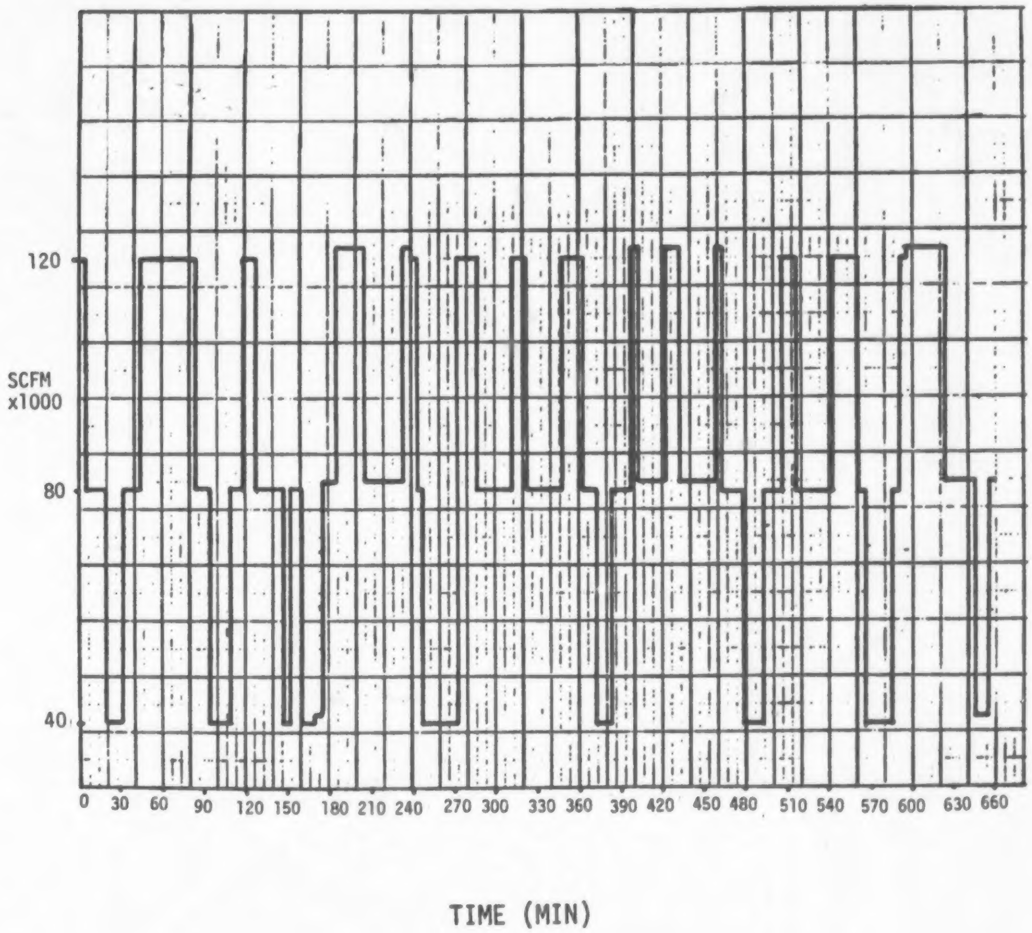
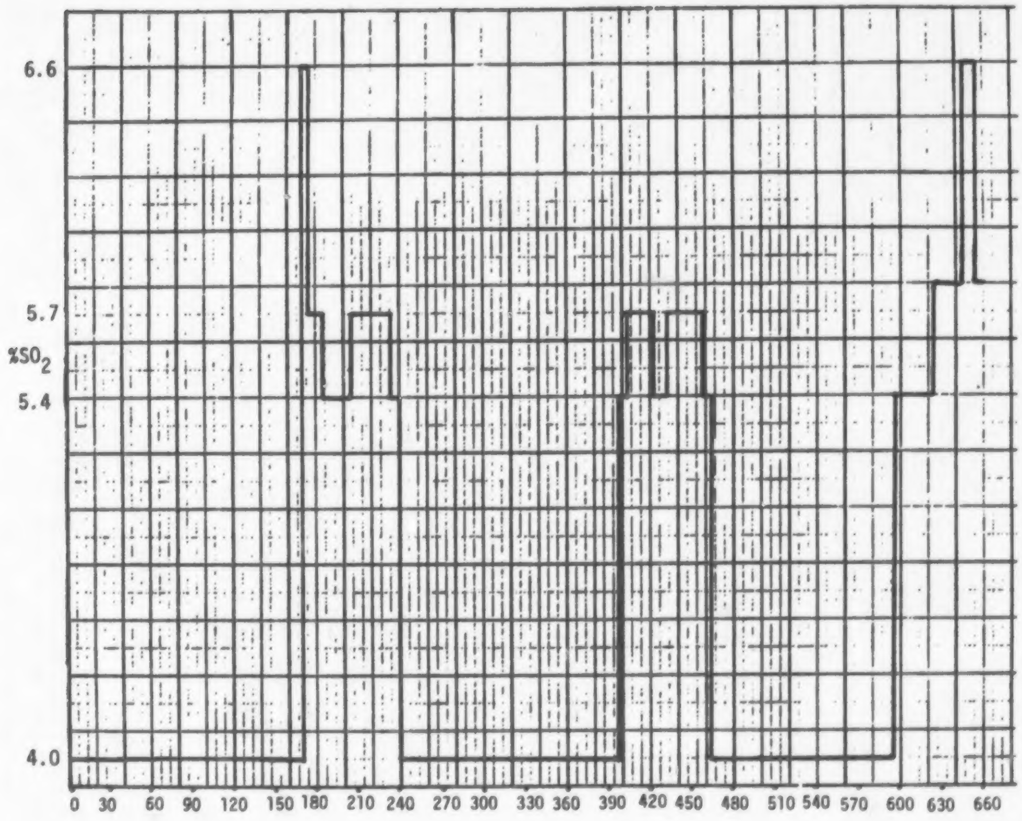


Figure H-3. Converter Offgas Volume vs Time Characteristics for Programming



TIME (MIN)

Figure H-4. Converter %SO$_2$ Offgas Characteristics for Programming

Table H-1. CONVERTER OFFGAS VOLUME AND SO_2 PROFILES

O_2 and no O_2 Enrichment					
Time (Min)	Percent (SO_2)	Volume (SCFM)	Time (Min)	Percent (SO_2)	Volume (SCFM)
5	4.0	120,000	25	4.0	80,000
15	4.0	80,000	15	4.0	120,000
11	4.0	40,000	10	4.0	80,000
14	4.0	80,000	11	4.0	40,000
40	4.0	120,000	14	4.0	80,000
10	4.0	80,000	5	5.4	122,000
15	4.0	40,000	20	5.7	82,000
9	4.0	80,000	10	5.4	122,000
10	4.0	120,000	25	5.7	82,000
20	4.0	80,000	5	5.4	122,000
5	4.0	40,000	16	4.0	80,000
7	4.0	80,000	14	4.0	40,000
10	4.0	40,000	15	4.0	80,000
5	6.6	42,000	9	4.0	120,000
10	5.7	82,000	26	4.0	80,000
20	5.4	122,000	19	4.0	120,000
29	5.7	82,000	5	4.0	80,000
5	5.4	122,000	19	4.0	40,000
5	4.0	120,000	5	4.0	80,000
4	4.0	80,000	5	4.0	120,000
24	4.0	40,000	29	5.4	122,000
15	4.0	120,000	20	5.7	82,000
25	4.0	80,000	10	6.6	42,000
10	4.0	120,000	5	5.7	82,000

APPENDIX I

CONVERTER SLAG RETURN: ADVANTAGES AND DISADVANTAGES

More and more smelters are weighing the economic advantages and disadvantages of returning converter slag to the reverberatories. For those smelters which have been plagued by magnetite and its build-up in furnace bottoms or hearths and copper entrainment in furnace slags, the elimination of the magnetite source in the converter slag has resulted in much improved furnace conditions. Some smelters, generally using green feed, have been able to practice magnetite control in the furnaces and still prefer the return of hot converter slag to the furnaces.

Among the advantages of converter slag return to reverberatories are (13):

a. Retention of latent heat in converter slag for addition to furnace heat reserve.

b. Rapid chemo-thermal reaction of the slag constituents with the molten bath, resulting in an increased smelting rate.

c. Economic furnace separation of copper and precious metals in the converter slag while molten and their return to the matte in the furnace.

d. General economy of converter slag treatment and handling while still in the molten state.

e. Minimization of equipment involved in returning slag to the furnace as compared to the equipment required for the flotation process. For example, the power requirement for crushing and grinding is approximately 40 KWH per ton.

f. Cheaper disposal of undesirable elements by their elimination in the reverberatory slag.

g. Assistance in maintaining an open flow channel in the furnace bath from the bridgewall to the skimming end, washing away "floaters" and charge bridges. This is principally due to a slight rise in the bath elevation in the burner end when slag is received and which is eventually transmitted down through the length of the furnace to the skimming bay.

Among the advantages of not returning converter slag to the reverberatories are:

a. Elimination of most build-up of magnetite in the reverb-converter system and its many detrimental effects on hearth and bottoms, higher slag losses, additional fluxing required, higher slag temperatures required for separation, etc.

   Note: Part of the problem concerning magnetite is that there has been much difficulty encountered concerning routine percent determination by analytical methods. With the advent of modern laboratory equipment, this has become more rational and it is found converter slags normally contain 40 to 50 percent Fe (an easy laboratory determination) and that a larger percentage of the iron may be in the magnetite form than formerly thought. This can result in an analysis as high as 53 percent Fe_3O_4 in some cases.

b. Prevention of surges in gas flow at the furnace outlet, usually accompanied by increased SO_2 concentrations, caused by the rapid chemo-thermal reaction between the slag and the furnace bath.

c. The reduction of air infiltration from slag receiving-launder openings which causes undesirable cyclic presence of oxygen and reduction of SO_2 concentration in the furnace atmosphere. The volume of the furnace exit gases is also increased by this excess infiltrated air, resulting in greater heat loss from the furnace. Those problems are thus eliminated.

d. Elimination of the oftentimes excessive heat generation in the immediate contact area of converter slag and furnace bath, with accompanying splashing of the bath on bridge and sidewalls, causing damage to the brickwork.

e. Elimination of the higher labor and maintenance cost involved in the upkeep of slag return launders. Usually one operative furnace crewmember is required solely for launder cleaning on each furnace shift as well as some mechanical maintenance requirements.

f. Elimination of the high capital, upkeep and replacement cost of equipment involved and even more so if retractable launders are used.

g. Reduction of spillage of converter slag. Spillage requires that more reverts be smelted and that labor be involved in cleanup in the converter aisle.

h. Without slag return, fluxing requirements to treat the magnetite are lower resulting in less material passing through the furnace. Also, less reverberatory slag is produced (only half) and cost of disposal is proportionately lower. This results in lower copper-pound loss due to the decreased volume. In some locations the percentage of copper loss in the furnace slag is higher than normal, mainly due to the presence of excess magnetite. Copper content of furnace slags without converter slag returns have decreased as much as 0.2 percent.

APPENDIX J

OXYGEN ENRICHMENT EXPERIENCE AT THE CALETONES SMELTER

Experimental work on the use of oxygen in green feed reverberatory furnaces was started at the Caletones smelter in Chile in 1971. This development work was continued through to 1976. During this time, a gradual transition was made from supplying fuel conventionally through air-oil burners at the end of the furnace to totally through oxygen-fuel burners positioned over the furnace area and suspended from the roof.

Eventually one furnace was converted to 12 oxy-fuel burners installed through the roof of the furnace so that the flame impacted on the charge banks. A total of 380 long tons per day of oxygen allowed a smelting rate of 1,520 dry tons per day with decreased fuel consumption in the range of 0.81×10^6 Kcal.

Matte grade tended to increase from 38 percent copper before major use of oxygen enrichment to 49 percent copper with full oxygen usage. Copper in the slag reduced from 1 percent without oxygen enrichment to 0.7 percent with full oxygen. Another additional effect with the slag was noted that because of its higher temperature, it was possible to eliminate calcium carbonate used as flux (approximately 4 percent of the charge). The increase in matte temperature also minimized the furnace bottom buildup with magnetite. The smelting level and production increased significantly to values over 100 percent of those with no oxygen enrichment.

The most significant result from a pollution control standpoint was that the SO_2 concentration range in the offgases increased to

5.8 - 7.3 percent. This is sufficiently high, of course, to allow direct processing of the gases in a sulfuric acid plant.

It was necessary to use a bottom ventilation system when full oxygen was used for this reverberatory furnace. However, furnace wear on a per-ton of copper basis was either less or the same as previously encountered.

APPENDIX K-1

PROCESS DESIGN FOR DIRECT PROCESSING OF REVERBERATORY FURNACE GASES

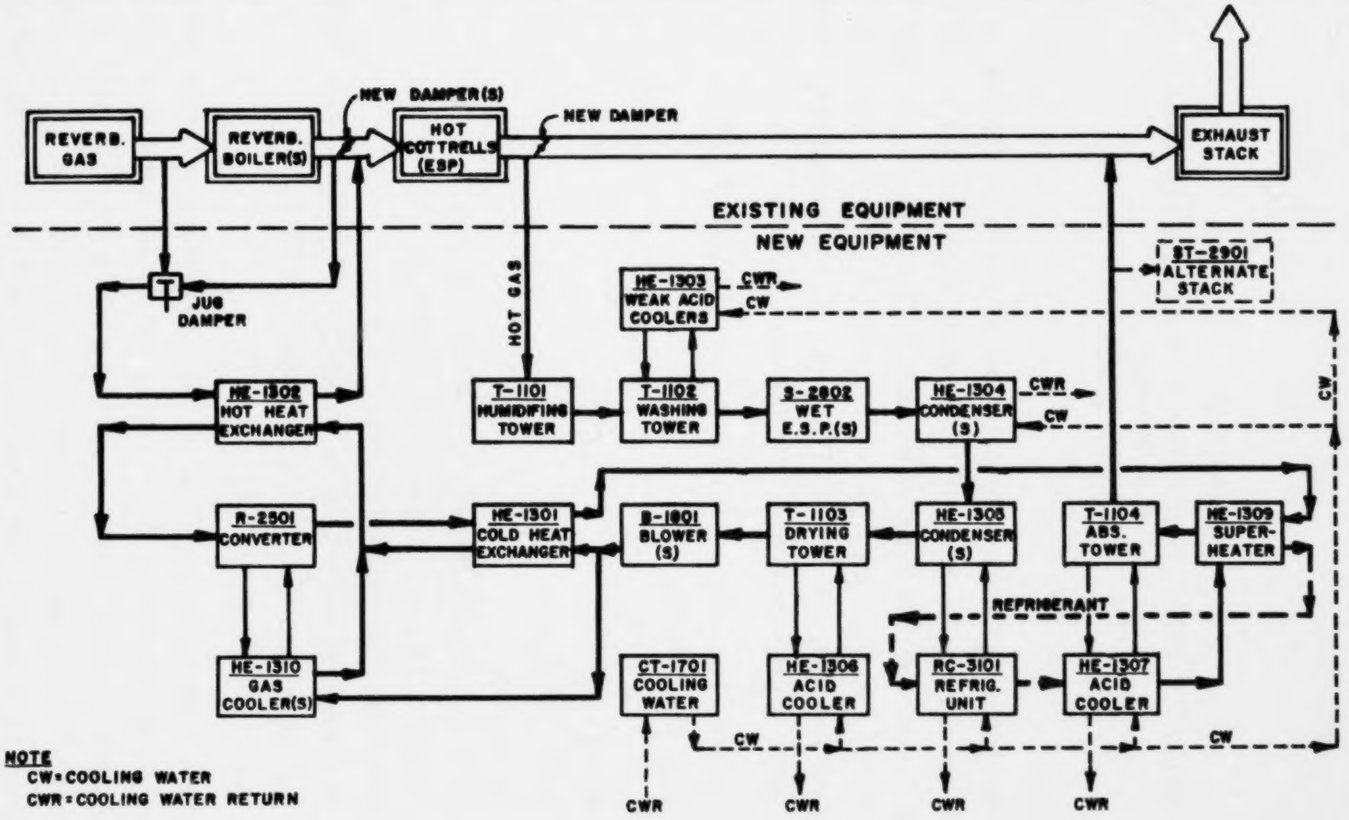
by Tim J. Browder
Tim J. Browder Company

K.1 GENERAL

The Browder reverberatory furnace gas sulfuric acid plant is designed in this study to produce 192.6 short tons per day of sulfuric acid (based on 100% H_2SO_4) for each 1.0% of SO_2 in the feed stream entering the SO_2 converter when operated at a maximum flow rate of 170,000 Nm^3/hr (100,000 SCFM) of dry gas to the converter. Assumed characteristics of the reverberatory furnace effluent are:

Volume Flow Rate - 170,000 Nm^3/hr (100,000 SCFM)
0.5% to 1.5% SO_2
2.0 - 9.0% CO_2
0.03% SO_3
4.0 - 20.0% H_2O
Balance N_2
Acid plant emission SO_2 = 450 ppm (maximum)
Assume acid plant adjacent to reverberatory furnace
Altitude 1525 meters (5,000 ft.)
Gas temperature out of reverberatory furnace 1200°C (2200°F)
Gas temperature out of W.H.B. 400°C (750°F)
Dust Load 50 grain/SCF

Figure K-1 presents the flow system. Metallurgical feed gas containing a weak stream of SO_2, O_2, CO_2 and N_2 and some acid mist in the presence of water vapor is collected from the exit side of a reverberatory furnace gas hot Cottrell precipitator and is conveyed in a gas flue to a humidifying tower. The humidifying tower humidifies and cools the gas and removes some of the particulate matter. The gas next passes to a washing tower in which further cooling of the


REVERB. GAS
REVERB. BOILER(S)
NEW DAMPER(S)
HOT COTTRELLS (ESP)
NEW DAMPER
EXHAUST STACK
EXISTING EQUIPMENT
NEW EQUIPMENT
ST-2901 ALTERNATE STACK
JUG DAMPER
HOT GAS
HE-1303 WEAK ACID COOLERS
CWR
CW
HE-1302 HOT HEAT EXCHANGER
T-1101 HUMIDIFING TOWER
T-1102 WASHING TOWER
S-2802 WET E.S.P.(S)
HE-1304 CONDENSER (S)
CWR
CW
CW
R-2501 CONVERTER
HE-1301 COLD HEAT EXCHANGER
B-1801 BLOWER (S)
T-1103 DRYING TOWER
HE-1305 CONDENSER (S)
T-1104 ABS. TOWER
HE-1309 SUPER-HEATER
REFRIGERANT
HE-1310 GAS COOLER(S)
CT-1701 COOLING WATER
HE-1306 ACID COOLER
RC-3101 REFRIG. UNIT
HE-1307 ACID COOLER
CW
CW
CWR
CWR
CWR
CWR
NOTE
CW=COOLING WATER
CWR=COOLING WATER RETURN

SIMPLIFIED FLOWSHEET OF REVERBERATORY GAS
SULFURIC ACID PLANT CASE II

TIM J. BROWDER COMPANY
Post Office Box 8473
San Marino, Calif. 91108, USA

Figure K-1

gas is accomplished by recycled cool liquor contacting the countercurrent flow of gas leaving the humidifying tower. After being washed to remove a large portion of the dust and some sulfuric acid mist, the gas passes to the wet ESP (electrostatic mist precipitators).

The gas passes from the mist precipitators to a series of condensers. In the first series of condensers, the gas is indirectly cooled in the condenser tubes using cooling water. The second series of condensers has a closed circuit refrigeration unit whereby chilled water is used to further condense the water vapor from the gas in order to achieve water balance before passing to the acid plant's drying tower.

The clean refrigerated gas, with the proper moisture content (water balance), then flows through the drying tower which removes the remaining moisture from the gas. The drying tower gas is then passed through a two-stage demister on the top of the drying tower and then flows to one operating (of two installed) main gas blower. The gas blower propels the gas through the plant to finally accomplish the manufacture of sulfuric acid.

The gas is next heated in order to be able to pass to the converter. The preheating of this gas is accomplished in two stages. The blower discharged gas is passed first into the top vestibule of a cold gas heat exchanger flowing down through the tubes. This gas is indirectly heated by a counter-current stream of hot gas leaving the converter. The gas which has then been preheated in the cold heat exchanger next flows to a hot heat exchanger before passing to the converter. The gas is thus indirectly heated to the converter catalyst ignition temperature in the hot heat exchanger with a stream of hot gas. The temperature of this gas is controlled by mixing reverberatory furnace offgas from upstream and downstream of the waste heat boiler. Mixing is accomplished in the jug damper (Figure K-2). The hot preheated gas at approximately 438°C (820°F) next passes into a multi-stage converter. The converter processes the SO_2 to SO_3. The gas leaving the converter stages is cooled as required before passing back into additional catalyst stages.

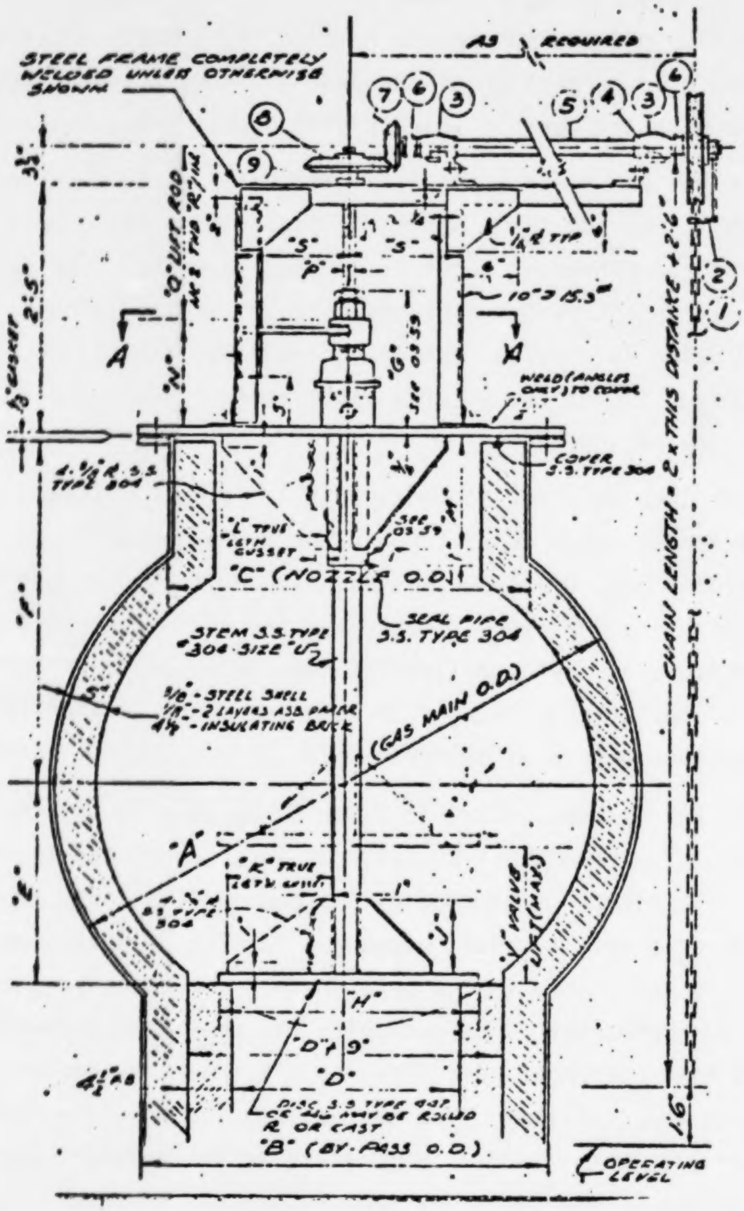

STEEL FRAME COMPLETELY WELDED UNLESS OTHERWISE SHOWN
AS REQUIRED
⑧
⑨
⑦
⑥
③
⑤
④
③
⑥
②
①
3½"
2'-5"
13" GASKET
"Q" LIFT ROD
"S"
"S"
"P"
¼" R TYP
10" ⊐ 15.3#
A
A
"N"
"G"
SEE DS 59
WELD (ANGLES ONLY) TO COVER
4-9/16" R S.S. TYPE 304
COVER S.S. TYPE 304
"L" TRUE LGTH GUSSET
SEE DS 59
"C" (NOZZLE O.D.)
SEAL PIPE S.S. TYPE 304
STEM S.S. TYPE 304 SIZE "U"
"F"
5"
3/8" - STEEL SHELL
1/8" - 2 LAYERS ASB PAPER
4½" - INSULATING BRICK
(GAS MAIN O.D.)
"A"
"E"
"K" TRUE LGTH GUSSET
B.S TYPE 304
1"
"J"
VALVE LIFT (MAX)
"H"
"D" + 9"
"D"
4½" AB
DISC S.S TYPE 430 OR 446 MAY BE ROLLED R OR CAST
"B" (BY-PASS O.D.)
CHAIN LENGTH = 2 x THIS DISTANCE + 2'-6"
1'-6"
OPERATING LEVEL

Figure K-2. Jug Damper Assemblies

From the final catalyst bed, the gas is then passed to the shell side of the cold heat exchanger where the gas is cooled to approximately 440°F before entering the Freon superheater and then flows to the absorption tower. The absorption tower absorbs the SO_3 from the gas and the remaining gas is then passed through a high efficiency demister (mist eliminator) and then vented to the atmosphere through an exhaust stack.

K.1.1 GAS CLEANING

K.1.1.1 General

Reverberatory gas which has been passed through the reverberatory furnace waste heat boilers and through a hot Cottrell to remove some of the particulate matter is diverted by a new damper installed in the main line to the humidifying tower. The gas is conducted through a carbon steel duct, which is externally insulated with rockwool blanket insulation, to the humidifying tower. The humidifying tower is a carbon steel vertical mounted vessel with conical bottom containing teflon and polypropylene linings. Inside of these linings are placed acid-proof brick lining unless the gas contains fluorine, then carbon brick will be substituted. The inlet nozzle of the tower which is close to the tower base and above the conical bottom is water jacketed and cooled in order to prevent stress problems from occuring in the steel shell. The hot gas enters this humidifying tower at approximately 370-400°C (700-750°F) through the gas nozzle, and turns and flows up through the empty tower. The tower shell contains a series of spray nozzles through which weak acidic recycled liquor is sprayed into the tower counter-current to the gas flow stream. This spraying of the liquor into the tower evaporates some of the water into the gas stream thereby humidifying the gas and reducing the temperature to approximately 66-68°C (150-155°F). The top dome of this tower also contains spray nozzles and emergency spray nozzles which are used in case of power or pump failure. These emergency spray nozzles allow the towers to have water sprayed continuously to prevent damage to the tower in case there is a power failure. The gas leaving the top of the tower is then conveyed down through fiberglass reinforced plastic (FRP) duct in where there is a swirler knockout to reduce the mechanical water droplet carryover from the humidifying tower. The gas then enters a washing tower for further cooling and further removal of dust and acid mist. The gas which has been cooled to approximately 66-68°C (150-155°F), then flows up through the washing tower which contains 3-1/2 x 3 1/2 inch plastic (PPE) Pall Rings. Over this tower is circulated weak recycled cooled liquor which accomplishes further scrubbing (washing) of the gas to remove particulate matter, and acid mist which is present in the gas, before passing to the wet electrostatic acid mist.

The down flowing acidic liquor leaving the washing tower is pumped through a series of Carbate coolers to remove the heat that has been recovered in the washing tower. This heat removal occurs as a result of water vapor being condensed from the gas. This water vapor has previously been added to the gas as a result of humidification in the previous humidifying tower.

K.1.1.2 Acid Mist Precipitators

The scrubbed, humidified and washed process gas then passes through the acid mist precipitator system. The electrostatic type acid precipitators are comprised of lead tubes with a lead covered electrical charging wire located in the center of each tube. The processed gas passes up through the annular space between the center wire and the tube. Liquid acid droplets and particles are electrostatically charged and are collected on the inner surface of the tube and drained to the bottom of the precipitators. The acid mist precipitators are equipped with water sprays which may be used to clean the precipitator tubes while the plant is in operation. Effluent is then directed to an acidic disposal system outside of the battery limits of the plant.

K.1.1.3 Gas Dehumidification by Cooling

The clean process gas then flows to two sets of condensers. The gas leaving the acid mist precipitators is conveyed in an FRP duct into the top section of the condensers. The condensers are vertical shell and tube Carbate units in which the saturated gas enters the top FRP vestibule flowing down through the Carbate tubes. Cooling is accomplished in the first set of condensers using cooling water recycled from a cooling tower outside of the plant's battery limits. The gas is then collected in the bottom vestibule of the first set of condensers and condensate is separated from the gas. The gas is then conveyed through an FRP duct and to the second bank of condensers. The second bank of condensers contains a closed circuit refrigeration unit in which chilled water is used to further reduce the gas temperature in the condensers to approximately 7OC (45°F) before passing to the drying tower in the sulfuric acid plant.

K.1.2 REVERBERATORY FURNACE SULFURIC ACID PLANT

K.1.2.1 Drying Tower

The clean wet feed gas from the gas cleaning plant is now drawn to a packed drying tower over which 94% sulfuric acid is circulated in order to completely dry the gas. The dry SO_2 gas leaves the drying tower through a two stage demister (mist eliminator) located in the top of the drying tower. The 94% sulfuric acid for the drying tower is supplied from the drying tower sump and flows by gravity to the drying tower pump tank from which it is recirculated by an acid pump to the top of the drying tower weirs from the drying tower acid coolers. Since the acid in the drying tower is continuously being diluted, the strength of this acid is maintained by cross-transfering the required amount of strong 98.5% acid from the absorption tower system to the drying tower pump tank. The change of level that results from the cross-transfer is controlled automatically by level control instrumentation and valving.

K.1.2.2 Drying Tower Demister

The drying tower demister consists of two horizontal pads of teflon media supported by CA-20 grids. These horizontal pads are located in a chamber mounted directly on top of the drying tower. The purpose of these demisters is to eliminate any acid mist carry-over from the drying tower and to protect the blower and the remaining down stream equipment in the acid plant from corrosion.

K.1.2.3 Main Gas Blower

The clean-dry process gas which has been pulled through the system and through the drying tower demisters now enters one of two main gas blowers (one blower being a spare). These blowers supply the necessary pressure for the gas to flow through the remaining equipment in the acid plant. The suction and discharge lines of the blowers are carbon steel ducts which are normally only painted externally and not insulated. The gas then flows from the blower into the heat exchangers, to be preheated to allow the gas to obtain the proper catalyst ignition temperature, before being passed to the converter system.

K.1.2.4 Cold Heat Exchanger

The cold heat exchanger is a vertical carbon steel vessel mounted on steel grillage. The blower discharge gas enters the top vestibule of this cold heat exchanger flowing down through the tubes thereby being preheated in a counter-current flow with hot gas exiting the last stage of the converter which is passed on the shell side across the tubes of the heat exchanger. The gas leaves this heat exchanger and then flows to a shell side of the hot heat exchanger. This entire cold heat exchanger is constructed of carbon steel plate with internal aluminized parts and contains a top and bottom tube sheet with the necessary carbon steel tubes. Additional service life can be obtained from this heat exchanger by using Alonized tubes. This heat exchanger is insulated with two inches of rockwool insulation on the outside, and in addition contains weather seal protection. The blower discharge duct leading into the top vestibule of this heat exchanger is carbon steel. The hot gas leaving the lower vestibule of this cold heat exchanger passes into a duct which is aluminized, and the gas is conveyed through this duct over to the hot heat exchanger.

K.1.2.5 Hot Heat Exchanger

The hot heat exchanger is a specially designed vertical unit which allows the gas which has been previously heated in the cold heat exchanger to flow on the shell side of the hot heat exchanger up across a series of tubes, leaving the top of the shell side of the heat exchanger and then flowing to the converter. This gas is heated counter-currently with mixed hot gas exiting the reverberatory furnace and waste heat boilers. The top vestibule of this heat exchanger contains refractory to protect the heat exchanger from extremely high temperature which can be encountered on startup since this unit is also used as a preheater during startup operations. This heat exchanger has a special bottom vestibule with a conical bottom and contains the tubes extended out approximately six feet beyond the lower tube sheet to act as knockouts for any course dust which is conveyed down through the pipes. The conical bottom of the heat exchanger acts as a collection device and contains two double weighted valves to remove any dust which settles out in the bottom of this conical hopper. The heated gas is then conveyed to the converter. This is accomplished in a carbon steel duct externally insulated and internally aluminized.

K.1.2.6 Converter

The previously preheated clean dry process gas enters the top bed of the converter and passes down through a series of vanadium pentoxide catalyst beds. The process gas, after being heated as a result of the exothermic reaction that takes place in the catalyst bed, leaves the converter chamber and passes externally to the horizontally-mounted gas cooler on the side of the converter.

The gas, after passing across the tubes of this gas cooler, returns to an additional catalyst bed and then flows through this bed where further conversion takes place with some slight temperature rise. The gas from other successive beds may also be heated as a result of this exothermic reaction and cooling with gas coolers as required. Gas finally leaves the bottom of the converter and flows to the lower shell side of the previously mentioned cold heat exchanger.

The catalyst bed design considerations must include the conditions generated by the plant duty cycle. Turn down ratio of 170,000 Nm^3/hr (100,000 SCFM) system design herein may be as low as 40% over a range of SO_2 concentration from 0% to 2.5%. Reverberatory furnace SO_2 emission concentration will vary in relation to charge frequency with maximum SO_2 occurring at the time the charge is dropped. Some furnaces have been known to generate peak SO_2 concentrations considerably above 2.5% but usually for only periods of 2 to 5 minutes.

The large duct volumes downstream of the furnace will tend to mix the high concentration to more nearly the average values of 0.5 to 1.5%. The catalyst tends to adsorb SO_2 and will serve as a "sink" under short term peak conditions to minimize acid plant peak emissions. The catalyst and steel in the converter and associated ductwork will serve as a thermal "sink" to minimize temperature peaks so that the heat exchanger system operation will not be effected to any great extent. If, despite the above, SO_2 surges do effect the plant operation, additional catalyst can be added (it should be noted that a large extra quantity has been included in the present design to provide an operating margin).

The converter is a vertical carbon steel vessel mounted on steel grillage beams and contains a dish top head. The internal beds of the converter are supported by a vertical cast iron post. Each catalyst bed consists of catalyst and quartz, and is supported on triangular cast iron grid sections which in turn are supported by the cast iron post. The internal surface of the converter is completely aluminized to protect the converter shell from scaling. The external surface of the converter contains four inches of rock-wool blanket insulation and is protected from the weather by weather seal.

K.1.2.7 Absorption Tower

The SO_3 gas, after leaving the final stage of the converter, passes to the shell side of the cold heat exchanger. The converter exit gas is cooled by the blower discharge gas inside the tubes of the cold heat exchanger. The gas at approximately 221-227°C (430-440°F) is then passed to the Freon superheater and then to the absorption tower. The SO_3 is removed in the absorption tower by 98.5% sulfuric acid continuously recycled over this tower and down through the packing. The acid leaves the bottom of the absorption tower and flows to an acid pump tank. From the pump tank, the acid is conveyed by one of two installed pumps (one being a spare), and conveyed to the acid coolers to remove the heat generated in the tower before the acid flows back to the top of the absorption tower. The absorption tower is similar to the drying tower and contains cast iron acid distributors.

K.1.2.8 Absorption Tower Demister

The top of the absorption tower contains a high efficiency demister, usually a York type SA. This unit will remove any acid mist which has been formed previously in the system and return it as droplets to the absorption tower to be recovered.

K.1.2.9 Stack

The residual gas leaving the absorption tower is conveyed in a carbon steel duct leading to a vent or exhaust stack. The gas is then discharged to the atmosphere. The SO_2 concentration of this gas will be less than 300 parts per million at all times when initially starting with 1% SO_2 gas. The gas, however, may be ducted back to the original flue and put into the main exhaust stack for the smelter if required.

K.1.2.10 Acid Pump Tanks and Pumps

In order to maintain sufficient acid quantity and to maintain the required strength in both the drying and absorption tower system, pump tanks are included. The pump tanks serve as a surge volume and also contain the acid which will be recirculated over the towers. The drying tower pump tank contains two acid pumps. One pump is a spare. The acid flows from the towers into the pump tanks. The acid is then pumped through a cast iron pipe to the acid coolers and from the acid coolers back to the tops of the towers. The absorption tower pump tank is similar in design to the drying tower pump tank.

K.1.2.11 Acid Cooler System

Each acid system contains a separate pump tank and recirculating pumps as well as separate acid coolers. The acid cooler system consists of a horizontal stainless steel shell and tube unit. The acid flows through the tube side of the acid cooler and Freon is on the shell side.

K.1.2.12 Acid Product Transfer and Drain

Product acid is pumped to OBL (outside battery limits) and into an acid storage area. The product pump also serves as a spare for the drain pump which may be used to drain and pump acid from the system for servicing or for maintenance.

K.2 OUTSIDE BATTERY LIMITS (OBL) PLANT FACILITIES

K.2.1 COOLING TOWER

A three cell double cross-flow cooling tower is designed to accommodate the cooling loads for the weak acid scrubber system, the coolers for the drying and absorption tower systems, the condensers and refrigeration unit for the plant. The cooling tower is normally not considered a portion of the process part of the acid plant and is usually therefore outside battery limits (OBL) of the plant. The cooling tower is usually constructed of wood and mounted on a concrete water sump base. The cooling water after accomplishing its function of cooling various components in the plant is pumped while still under pressure to the top of the cooling tower and flows down a series of grids to the bottom of the tower. Air is conveyed through the bottom of the tower and flows crosswise to a center phleum section and vented out through propellers mounted on the top of the cooling tower.

K.2.2 COOLING WATER PUMPS

The cooling water pumps are mounted in a sump adjacent to the cooling tower. There are three cooling water pumps, normally two in operation, with one spare. The two pumps circulate the cooling water from the base of the cooling tower through the respective acid coolers, refrigeration unit, condenser, and weak acid coolers. The water is then returned to the top of the cooling tower.

K.2.3 PRODUCT STORAGE TANKS, LOADING PUMPS AND ASSOCIATED EQUIPMENT

The processed loading system tanks and other units are normally outside of the battery limits of a sulfuric acid facility and many times are not included in the process design since many companies already have acid storage systems.

K.3 PROCESS GUARANTEES

Sulfuric acid plants are usually guaranteed based on the production of sulfuric acid for a fixed gas flow and for a fixed percent gas strength. For varying gas flows and varying gas strengths, the usual design then encompasses the maximum gas flow and the maximum gas strength in order to establish the required quantity of catalyst to be charged to the converter. The reverberatory furnace gas sulfuric acid plant which, for this analysis, contains a maximum of 1.5% SO_2 is based on a design total gas flow rate of 170,000 m^3/hr (100,000 CFM) which requires about 165,000 liters of catalyst. A catalyst manufacturer would supply the catalyst guaranteed based on the gas flows, pressures, altitude and operating conditions both in flow and SO_2 concentration of the gases. Appendix K-3 includes a typical computer run showing these calculations, the stack gas analysis, and the required catalyst loading and operating temperatures for such an installation.

Under the conditions of the design of reverberatory furnace gas plants, it is very easy to obtain stack gas effluent of less than 450 parts per million in most cases and with low gas strengths the stack gas could be as low as 50 parts per million with a single contact system.

K.4 MECHANICAL DESIGN

K.4.1 GENERAL

This section presents a brief description of mechanical design, major equipment and supplementary facilities proposed for the reverberatory gas sulfuric acid plant. The design data represented herein and included in Appendix K-2 are based on the plant operated at an average flow of 170,000 Nm^3/hr (100,000 SCFM) of clean dry gas entering the sulfuric acid plant converter and when supplied with all utilities and materials required at the use condition with the proper proportion of sulfur dioxide, oxygen, and water. Design, fabrication and installation of the equipment and facilities is in accordance with the standard practices of the sulfuric acid industry and OSHA standards. A material list is included in Table K-1 and utility requirements are summarized in Table K-2.

TABLE K-1

REVERBERATORY FURNACE GAS
SULFURIC ACID PLANT
(100,000 SCFM)

EQUIPMENT LIST

ITEM NO.	SERVICE	DESCRIPTION
Towers		
T-1101	Humidifying Tower	18 - 0" dia. x 40'0" with Cone Bottom, Carbon Steel, Teflon, Ppe and Carbon Bricklining.
T-1102	Washing Tower	22' - 0" x 36' - 0" High, FRP
T-1103	Drying Tower	20 - 0" dia. x 25' - 0" High, C.S., Teflon, and Acid Proof Bricklined. Double Gas Inlet Nozzles
T-1104	Absorption Tower	20 - 0" dia. x 25' - 0" High, C.S., Teflon, and Acid Proof Bricklined. Double Gas Inlet Nozzles
T-1105	Lime Silo	6' - 0" dia. x 30' - 0" High, C.S. with 5 HP feed screw
Heat Exchangers & Coolers		
HE-1301	Cold H.E.	4,000 1 1/2" dia. tubes, 10 BWG,

Table K-1 (continued)

ITEM NO.	SERVICE	DESCRIPTION
		C.S. 30' - 0" long. Shell 13' - 6"
He-1302	Hot H.E.	1,000 - 3" dia. tubes, 14 BWG C.S., 30' - 0" Long, Shell, 12 - 0" dia. (Stainless Steel Tubes)
HE-1303	Weak Acid Coolers	Impervious Graphite Tubes 7/8" I.D., Steel Shells, 12,000 Sq. Ft.
HE-1304	Condensers (Water Cooled)	Impervious Graphite Tubes 7/8" I.D., Steel Shells - 24,400 Sq. Ft.
HE-1305	Condensers (Refrigeration)	S.S. Tubes - Steel Shell - 16,700 Sq. Ft.
HE-1306	Drying Tower Cooler	Chemetics - 500 Sq. Ft. S.S., Anodically Protected
HE-1307	Absorber Cooler	Chemetics - 2,100 Sq. Ft. S.S., Anodically Protected
HE-1308	Product Acid Cooler	Chemetics - 200 Sq. Ft. S.S., Anodically Protected
HE-1309	Superheater	3000 Sq. Ft.
HE-1310	Converter Gas Cooler	2750 Sq. Ft.
Pump & Drives		
P-1501A&B	Humidifying Tower (2)	3,600 GPM - 100' TDH 200 HP
P-1502A&B	Washing Tower Pumps (2)	5,500 GPM - 150' TDH 350 HP
P-1503A&B	Drying Tower Pump	Lewis Size 7, - 2,000 GPM 100 HP

Table K-1 (continued)

ITEM NO.	SERVICE	DESCRIPTION
P-1504A&B	Absorber Pump	Lewis Size 7, 2,000 GPM 100 HP
P-1505A&B	Product & Drain	200 GPM, 120' TDH, 15 HP
P-1506A&B	Neutralization Tank (2)	200 GPM, 100 TDH, 10 HP
P-1507 A,B, & C	Cooling Water Pumps	7,000 GPM, 130' TDH, 250 HP
Cooling Towers		
CT-1701	Cooling Tower	13,000 GPM, 190 MM BTU/Hr. (106.2 - 77°F.) 150 HP
Blowers		
B-1801 A,B,	Main Gas Blowers	100,000 SCFM, 7.03 psi delta P, 4,500 HP Each
Tanks		
TK-1901	Humidifying Tower Pump Tank	20' - 0" and 14' - 0" x 10 Deep
TK-1902	Seal Pot	6' - 0" dia. x 5' - 0" Deep
TK-1903	Drying Tower Pump Tank	22' - 0" dia. x 8' deep Teflon & A.P. bricklined
TK-1904	Absorber Pump Tank	22' - 0" dia. x 8' deep Teflon & A.P. brick-lined
TK-1905	Neutralization Pit (Tank)	16' - 0" x 16' - 0" x 10' deep

Table K-1 (continued)

ITEM NO.	SERVICE	DESCRIPTION
Reactors		
R-2501	Converter	40' - 0" dia. x 48' - 0" High, 4 Catalyst Beds
Separation Equipment		
S-2801	Gas Liquid Separator FRP - Integral in Duct	
S-2802 A, B, C, D, E & F	Electrostatic Precipitators (Each 2 Series)	158 tubes x 17' - 0" dia. 3 Parallel = 6 Total
S-2803	Drying Tower Demister	18' - 0" dia. - 2 Stage 1 - 18' dia. pad & 1-16' dia. pad
S-2804	Absorber Demister	York Type S,17' - 0" dia.
S-2805	Neutralization Tank Mixer	3 HP
Stack		
ST-2901	Stack	12' - 0" dia. x 149' - 0" High Self Standing-Spoilers at Top 20'
Refrigeration Cooler		
RC-3101, A,B,C.	Water Chillers	York, Open Turbopak - 3 Units (1500 Tons Total)
RC - 3101, A,B, & C	Water Chillers	York, Open Turbopak - 3 Units (1,500 Tons Total)
F-3101	Preheater Furnace	6' x 20' Bricklined

TABLE K-2

UTILITIES

REVERBERATORY FURNACE GAS
SULFURIC ACID PLANT
(100,000 SCFM GAS FLOW)

REV = 0
9-30-76

Sulfuric Acid Plant Case I

	Motor List	
Name	Connected	Average Operating
Lime Silo Feed Screw	5	3
Humidifying Tower Circ. Pump	200	180
(Spare)	200	---
Washing Tower Circulating Pump	350	300
(Spare)	350	---
Neutralization Tk. Pumps (Sump)	10	6
(Spare)	10	---
ESP - Seals Fans	(3) 3/Each	6 Total
Drying Tower Pump & Spare	100 (2)	70
Absorption Pump & Spare	100 (2)	75
Main Gas Blower	4,500	3,700
(Spare)	4,500	-----
Start-up Lubr. Pumps (Main Blower)	10	-----
(Spare)	10	-----
Drain (Product) Pump	15	12
(Spare)	15	--
Blower Room Exhauster	2	1 1/2
Utility Air Compressor	20	5
	10,606 HP	4358.5 HP
6 Mist Precipitators	(3) 50 KVA/ Each	90 KVA Total
Acid Plant (No Control Room, No Lights, No Cooling Tower) (A)	Connected	Connected
Normal Average (Acid Plant)	10,606 HP (150 KVA)	4358.5 HP (90 KVA)

Table K-2 (continued)

Name	Connected	Average Operating
Water Cooling Tower		
C.T. Well Pump (7,000 GPM)	250	200
C.T. Well Pump (7,000 GPM)	250	200
Spare	250	---
Cooling Tower Fan	150	100
Cooling Tower Fan	150	100
(B)		
	1,050 HP	600 HP
Control Room (Motors)		
Instruments	16 x 1/8 = 2	1 1/2
Air Conditioning (Heating)	20	10
(C)		
	22 HP	11.5 HP
Total Plant Lighting		
(D)		
All Lights	100 KW	60 KW

K.5 GAS CLEANING AND CONDITIONING PLANT

- Process Gas Inlet Flue Connection

Gas after passing through a hot Cottrell precipitator, is diverted by a new damper through a carbon steel externally insulated duct into the humidifying tower, (see Appendix K-1, page K-39).

- Humidifying Tower, T-1101

The purpose of the humidifying tower is to saturate and cool the dirty reverberatory gas before this gas enters a packed washing tower. Gas flows into the bottom of the empty humidifying tower and upwards against a series of spray nozzles circulating liquid counter-current to the up flowing gas stream. The bottom of the tower has a conical bottom which collects the recycled liquid which feeds an FRP pump tank which in turn feeds the rubber lined recirculating pumps. The liquor is then recycled back to the spray nozzles in the walls and top dome of the humidifying tower. This tower is a vertical carbon steel vessel, teflon line, polypropylene (PPE) lined and acid proof brick lined. If the gas contains fluorine, the brick lining will be carbon or graphite brick, otherwise if weak acid is used, standard acid proof brick is the construction material of this tower. The hot gas inlet nozzle of the tower will be externally jacketed and cooled with cooling water.

- Washing Tower, T-1102

Construction of this tower usually is of fiber glass reinforced plastic (FRP). The gas inlet nozzle is in the lower section of this vertical tower and the tower contains approximately 10 feet of packing consisting of 3-1/2 x 3-1/2 inch PPE Pall Rings. The top of the tower has a series of spray nozzles which allow weak liquor or water to be sprayed into the top of the tower and distributed uniformly over the packing. The washing of the gas occurs as the gas flows up through the packing and contracts the recycled cooled liquor flowing down over the packing. The liquor is collected in the bottom of the tower and is pumped by external rubber lined pumps through a series of carbate coolers and recycled back to the top of the tower.

- Acid Mist Precipitator (Electrostatic Precipitators) (S-2802, A, B, C, D, E, and F)

The electrostatic acid mist precipitators will be the lead tubuler type, with structural steel supports, and frames.

The top high tension insulator compartments will be provided with air sweep seals. This equipment includes a total of three complete high voltage electrical sets, necessary transformers, rectifiers and automatic controls. A water spray flushing nozzle system is included to permit the unit to be flushed out (washed) and cleaned while in operation. The precipitators are arranged three in parallel flow, followed in series by three more in parallel flow, a total of six units. The overall operation and clearance efficiency for acid mist and dust carried into the unit is estimated in excess of 98% of the rated flow capacity of the unit.

- Condensers (HE 1304, HE 1305)

Two series of sets of parallel condensers are installed to lower the temperature of the gas to the required conditions in order to achieve the correct ratio of water to SO_2 (water balance). Design requirements have been calculated in Appendix K-1, page K-69 and condenser design on page K-74. The first set of parallel flow condensers are cooled with water recycled continuously from the cooling tower system. Cooling water requirement calculation has been included in Appendix K-1, page K-82. The second set of condensers are cooled with chilled refrigerated water in closed circuit with the refrigeration unit

The condensers are constructed of carbon steel shells with impervious graphite tube sheets and tubes. The top and bottom heads or vestibule of these vertically mounted units are FRP (fiberglass reinforced plastic) and the lower section of the vestibule contain a separating section to remove condensate leaving the system. The flow of the gas is down through the tubes. After the first bank of parallel condensers the gas is collected and passed by an FRP duct up to the top vestibule for down flow through the second bank of parallel condensers which are water chilled using refrigerated water. The design of the second bank of condensers is similar to that of the bank used in using cooling water as the cooling media.

The Allied-IHI Freon driven turbine system used to drive the refrigeration system in this analysis has had considerable plant experience by Ishikawajima-Harima Heavy Industries in Japan and the Allied Chemical Corporation.

K.6 SULFURIC ACID PLANT EQUIPMENT

- Drying Tower, T-1303

The drying tower is fabricated of carbon steel plate with minimal wall thicknesses of carbon steel as follows:

LOCATION	CARBON STEEL THICKNESS, INCHES
Shell	3/8
Bottom	5/8
Top	3/8

The bottoms and sides of the tower are lined with teflon sheet covering with a minimum of one layer acid proof brick over the entire tower; however, the bottom section up to just above the gas inlet nozzles will contain one additional layer of acid proof brick. The packed section is approximately six feet deep and consists of acid proof grid tile and special Intalock saddles or Cascade Minirings. The packed section is supported on acid proof brick arches. Acid distribution over the tower is accomplished using troughs and spouts fabricated of cast iron. One or more spouts are provided for each square foot of cross sectional area for the packed section. The drying tower is provided with a required number of nozzles and manholes, and mounted on the top of the tower is a two stage acid mist eliminator demister (S-2803). The flat bottom of the vertical tower is supported on steel high beam grillage which carries the load of the packed tower. The grillage allows the dissipation of heat from the bottom of the tower.

- Cold Heat Exchanger, HE-1301

The cold heat exchanger is a carbon steel vertical shell mounted on grillage and the unit contains 4,000-1-1/2 inch tubes, 10 BWG - 30 feet long. The entire shell is 1/2 inch thick carbon steel grillage and 1 inch thick tube sheets. The gas enters just above the top tube sheet in the top vestibule and flows down through the tubes. The cold gas is heated in the tube by the shell side upflow hot converter exit gas. The entire inner surface of the heat exchanger is aluminized. The external surface of the heat exchanger has 2 inches of rockwool blanket insulation and a weather seal to protect it from the weather.

- Hot Heat Exchangers, HE-1302

The gas which has discharged from the blower and passed through the cold heat exchanger for initial preheating, is passed out of the bottom vestibule of the cold heat exchanger into the lower shell side of the hot heat exchanger. The gas flows up around the tubes of the hot heat exchanger discharging at the top of the vertical heat exchanger just under the tube sheet. The exiting temperature of the gas leaving the hot heat exchanger is sufficient to reach the catalytic conversion temperature required in the converter. The hot heat exchanger is a vertical carbon steel vessel containing stainless steel tubes with the top and bottom tube sheets stainless steel. This unit contains 1,000, 3 inch diameter tubes, 14 BWG-24 feet long between the tube sheets, with 6 feet of extension into the lower vestibule to act as dust knockouts. The bottom vestibule of this heat exchanger is a conical bottom with a center collection nozzle and double dump valves to allow any trapped dust to be removed from the system. The entire inner surface of this heat exchanger is aluminized. The top vestibule is lined with 2-1/4 or 2-1/2 inches of insulated refractory to protect the vessel while it is used as a preheater (during startup). The entire outer surface of this heat exchanger is covered with 2-1/2 to 3 inches to rockwool blanket insulation and is normally installed inside of the building; however, if it is installed outside, it will also contain external weather seal.

- Converter R-2501

The converter is a vertical carbon steel vessel with a dish top head and flat bottom. The converter is provided with cast iron grillage grates to support the catalyst. The catalyst grates are supported by cast iron pipe columns to support a triangle grid grate section for heat catalyst bed. Each catalyst bed contains two inches of quartz above and below each catalyst bed to maintain and stabilize the catalyst.

Gas, leaving the hot heat exchanger HE-1302, enters the top dish head of the converter and flows down through the first catalyst bed passing to the outside, to an external cooler, and then returning to the second catalyst bed. There is a minimum of three catalyst beds in this plant. The internal surfaces of this converter vessel are aluminized and covered externally with rockwool blanket insulation and weather seal. Each catalyst bed contains sufficient catalyst to convert the gas to the required sulfur trioxide content. Each catalyst bed has two thermocouples to indicate and record bed temperatures and also contains pressure connections for taking the pressure drop across each catalyst bed.

- Catalyst

The catalyst is a vanadium pentoxide (V_2O_5) hard non-fusing low ignition type catalyst and is installed in the converter. This catalyst meets the conversion conditions required at the flow and the gas strength conditions.

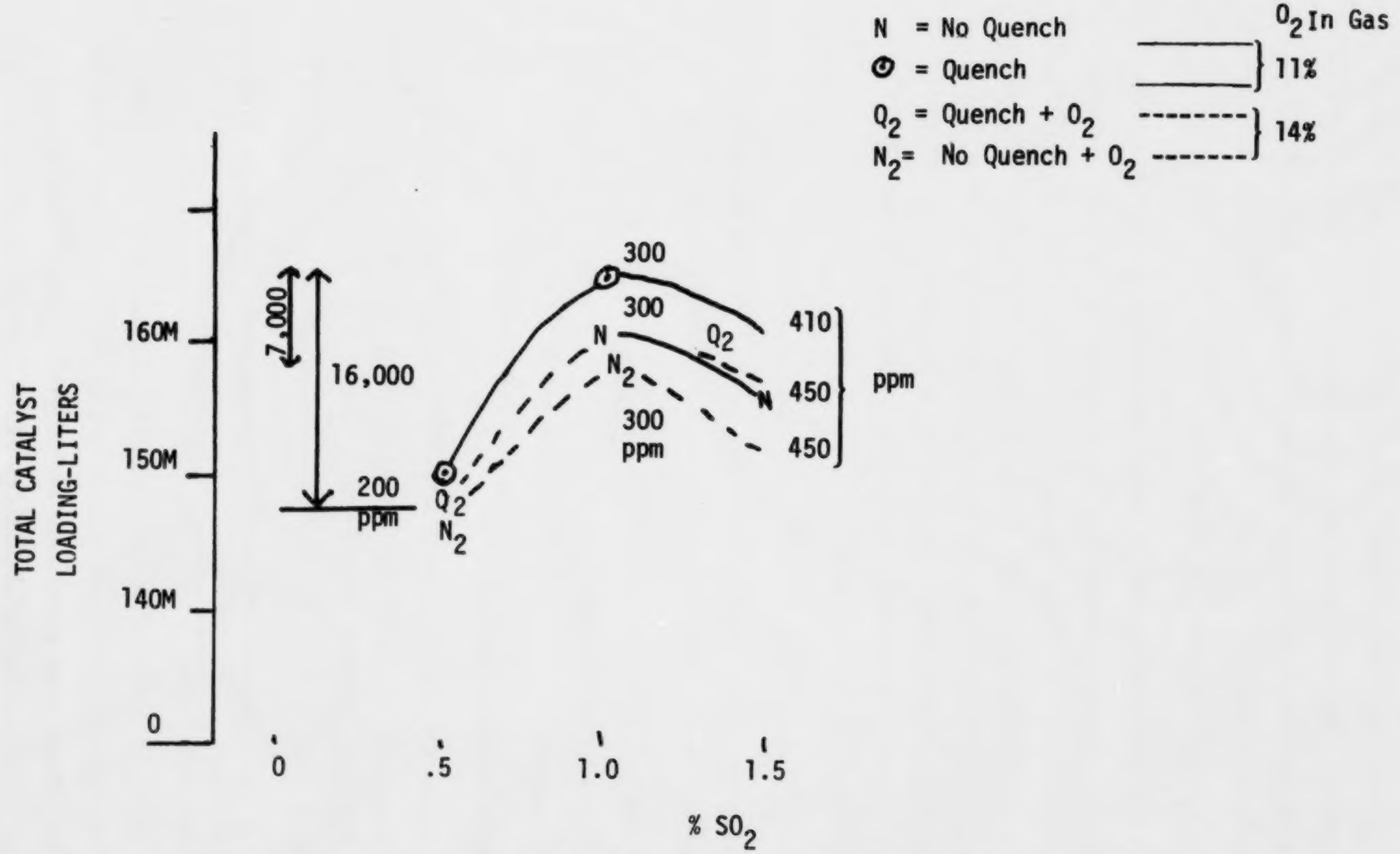
Twelve cases of catalyst information were computed by Catalyst and Chemicals, Inc. These various catalyst cases were computer run showing various gas strengths, oxygen contents and quench between catalyst beds. The catalyst data was selected on the basis of 0.5, 1.0, and 1.5% SO_2 gas with varying oxygen compositions of 11% and 14%. Also separate cases were used for by-passing cold gas around the first catalyst bed and using it for quench cooling. In each case it can be seen that the catalyst loading does not substantially affect the capital cost of the plant. The curve in Figure K-3 shows that the differential price of investment from one case to the next is only approximately a maximum of 25,000 dollars. This is based on using 16,000 differential liters of catalyst from one case to the next. Therefore, it can be seen that the effects of using quench gas in by-pass, or using oxygen for dilution, or for quenching has substantially very little effect on the capital cost of the plant. The design is made for a total of three catalyst beds to handle large fluctuations of gas.

- Absorption Tower, T-1104

The design of the absorption tower is similar to that used in the design of the drying tower. The difference will be the demister located in the top of the tower which is a high efficiency absorption tower demister (S-2804). This demister is a York type S unit.

- Pump Tanks, TK-1904

The pump tanks are constructed of 3/8 inch carbon steel plate. The tops and bottoms are flat. The bottoms and sides of the tank are lined with three or four mil thickness of teflon sheeting and a minimum of 3-3/4 inch course of acid proof brick. Each tank is supported vertically on steel grillage beams. The top of each tank contains two rectangular flanged nozzles to hold acid circulating pumps. One pump circulates acid continuously from the pump



$\therefore$ The worst case (Max. catalyst loading 165,000 liters, Quench 11% O_2 $\Delta\$$ = \$25,000
The next worst case ΔV = 71,000 liters. $\Delta\$$ = \$10,000 - Therefore NO Quench O_2
Suggest 3 catalyst beds, however.

Figure K-3. Data CCI Catalyst

tank through the coolers and over the tower and one pump is installed as a spare. The pump tanks each has manholes in the top and drain nozzles as required for the necessary piping, and instrumentation connections.

- Drying Tower Cooler, HE-1306

These coolers are stainless steel horizontally mounted units. The acid flows through the shell side diverted by baffles across the tubes. The cooling flows through the tubes. Each unit is individually anodically protected. The purpose of the acid coolers is to cool the acid which has increased in temperature as a result of flowing through the tower, and mixing with cross-transfer acid. The acid is pumped continuously from the pump tank through the cooler and over the drying tower.

- Absorption Cooler, HE-1307

The design of the absorption tower cooler is similar to that of the drying tower, however cooling is accomplished with Freon.

- Product Acid Cooler, HE-1308

This unit is considerably smaller but is similar in design to the above coolers.

- Converter Gas Cooler

The converter gas cooler is provided to compensate for possible maximum ranges of SO_2 entering the acid plant system from the reverberatory furnace. Normal operation in the 0.5 to 1.5% SO_2 concentration will not require this unit.

Design calculations are included in Appendix K-1, page K-84.

- Pumps and Drives

The pumps are listed on the equipment list, Table K-1. The pumps in the gas cleaning portion of the plant (front end) handling weak acidic liquor and solids are horizontal rubber lined slurry type pumps. The strong acid pumps used in the system are Lewis vertically submerged pumps that hang down into the pump tank.

Cooling water pumps are vertically hung pumps mounted in the coldwell. All the horizontal pumps have horizontal motors and vertical pumps have vertical motors.

K.7 EFFECT OF PLANT LAYOUT AND EQUIPMENT POSITION

In comparing Case I (Onahama) and Case II (Browder) it can be seen that one of the major differences results because in Case II a mixture of reverberatory boiler exit and reverberatory gases are mixed in the jog damper to give the required temperature entering the top vestibule of the hot heat exchanger. This scheme permits the use of the hot gas from the reverberatory to replace a fired furnace which has been used at Onahama (Case I), where weak gases have been encountered and autothermal conditions have not been achieved in sulfuric acid plants. The distance that the sulfuric acid plant can be removed from the reverberatory furnace is critical.

By reviewing known smelters, it can be seen that usually the reverberatory furnace building contains boilers and in these buildings there is usually sufficient head space adjacent to or above the reverberatory boilers to install gas-to-gas exchangers. The gas-to-gas exchangers normally would not occupy a circular space of more than 6 - 7-1/2 meters (20-24 feet) in diameter even for larger plants. These heat exchangers can be installed in a vertical position any place in a building adjacent to the reverberatory furnace or the reverberatory boiler.

In the past, sulfuric acid plants had been built essentially at one level, in which all of the equipment is installed at the ground level location. This is not necessary. Sulfuric acid plants could be built on more than one level, having the converter, cold heat exchanger and hot heat exchangers mounted adjacent to a reverberatory building or within the building itself and above the ground level. Location of the rest of the sulfuric acid plant is not critical and may be remotely placed. It is essential, however, that the acid plant converter hot heat exchanger and cold heat exchanger be adjacent to the reverberatory furnace when energy from reverberatory off gas is used. A typical case might be taking reverberatory furnace off gas from the exit of the Cottrell precipitator, further cleaning and humidifying it by passing through a wash tower, demisters, and condensors, and then ducting it to a drying tower adjacent to the absorption tower. The drying tower, demisters and blowers could be somewhat removed from the reverberatory furnace. The gas could then be passed through a duct to a cold heat exchanger, hot heat exchanger and the converter in an area in the reverberatory building. The gas leaving the cold heat exchanger could be re-piped some distance back into the absorption tower and then vented to the atmosphere through a stack.

If this scheme, using the converter hot and cold heat exchanger adjacent to the reverberatory furnace, is not used and these three components are isolated from the reverberatory building, then the system used at Onahama would apply, i.e., the hot heat exchanger would have to be fired with an auxilliary combustion furnace supplying the heat for the final pre-heating of the gas going to the converter. In each and every plant, it is not known if the flow scheme in Case II could definitely be used. Each would have to be reviewed on a case by case basis to determine if the converter, hot, and cold heat exchangers could be located adjacent to or inside of the reverberatory building. There is even a possibility where low head room buildings exist that extensions of the column line could be made and the converter and heat exchangers located on top or above the building.

Plan views of Case I (Onahama) and Case II (Browder), to scale are shown in Figures K-3a and 3b.

K.8 COST

While it is not the object of this project to include detailed cost estimates, a brief comment on installation schedule and system

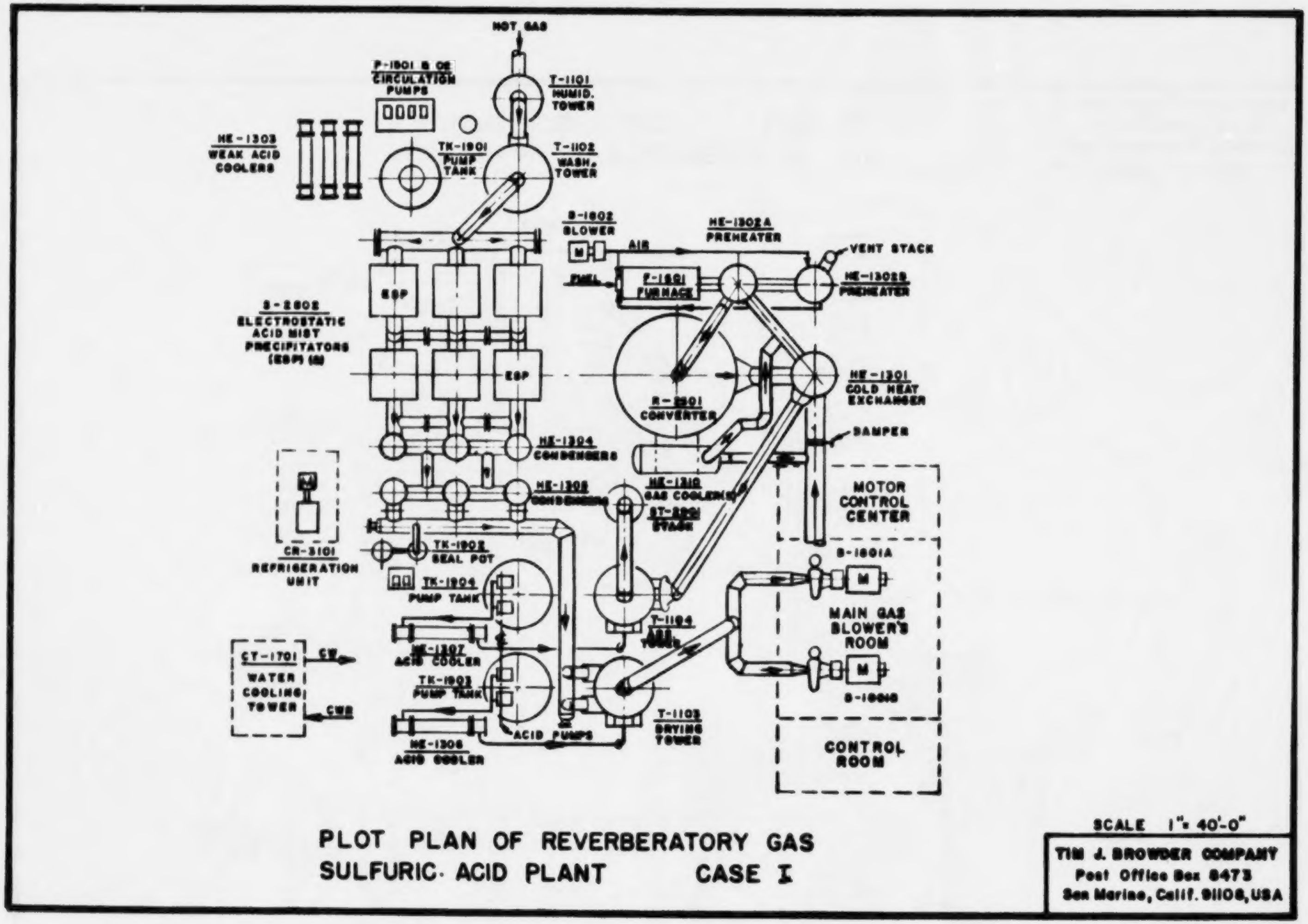
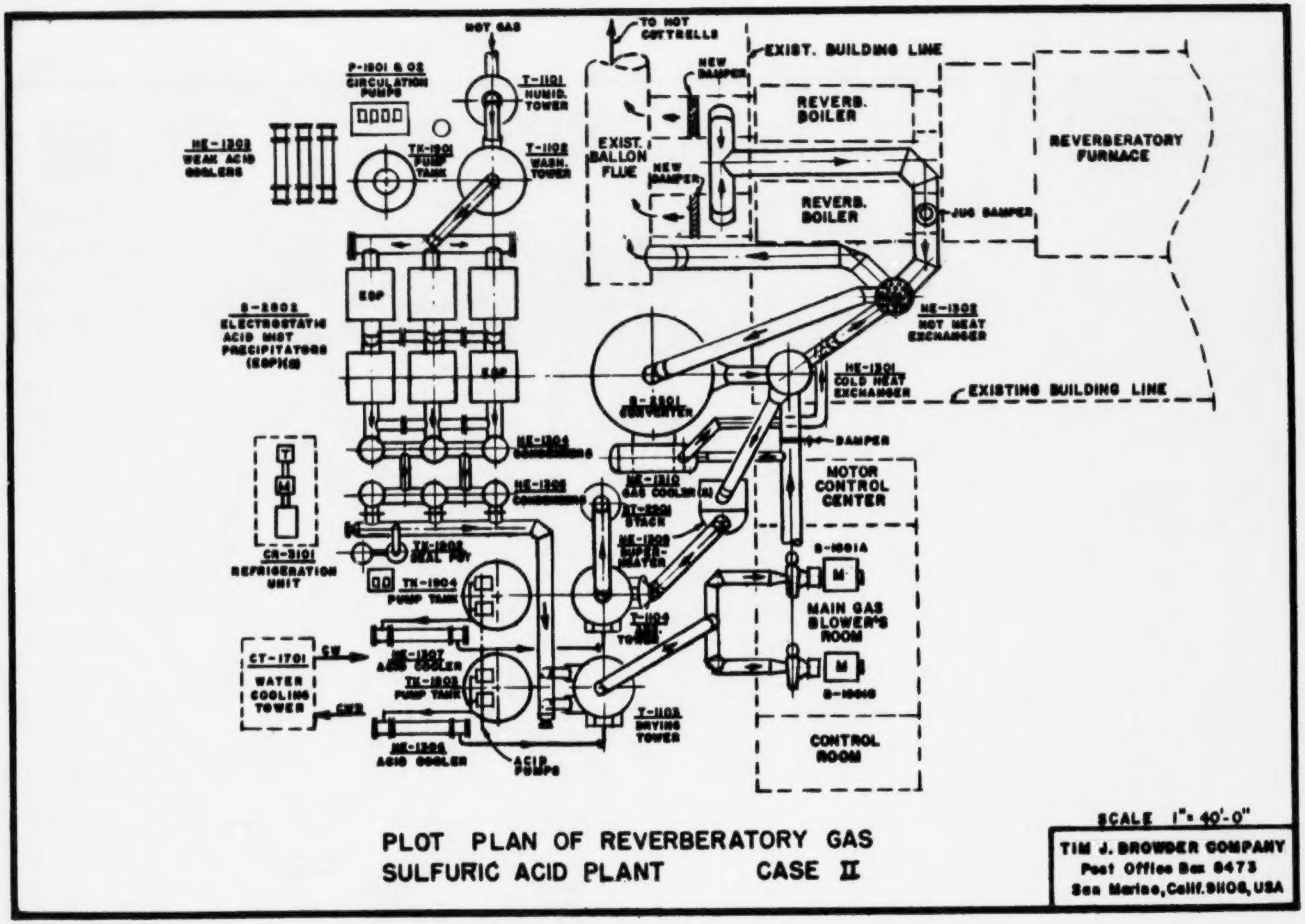

HOT GAS
P-1901 & 02 CIRCULATION PUMPS
T-1101 HUMID. TOWER
HE-1303 WEAK ACID COOLERS
TK-1901 PUMP TANK
T-1102 WASH. TOWER
B-1802 BLOWER
M
AIR
HE-1302A PREHEATER
VENT STACK
FUEL
F-1901 FURNACE
HE-1302B PREHEATER
ESP
ESP
B-2802 ELECTROSTATIC ACID MIST PRECIPITATORS (ESP) (6)
R-2301 CONVERTER
HE-1301 COLD HEAT EXCHANGER
DAMPER
HE-1304 CONDENSERS
HE-1305 CONDENSERS
HE-1310 GAS COOLER(S)
ST-2901 STACK
MOTOR CONTROL CENTER
CR-3101 REFRIGERATION UNIT
TK-1902 SEAL POT
TK-1904 PUMP TANK
B-1801A
T-1104 ABS. TOWER
MAIN GAS BLOWER'S ROOM
CT-1701 WATER COOLING TOWER
CW
CWR
HE-1307 ACID COOLER
TK-1903 PUMP TANK
ACID PUMPS
HE-1306 ACID COOLER
T-1103 DRYING TOWER
B-1801B
CONTROL ROOM
SCALE 1" = 40'-0"
PLOT PLAN OF REVERBERATORY GAS
SULFURIC ACID PLANT CASE I
TIM J. BROWDER COMPANY
Post Office Box 8473
San Marino, Calif. 91108, USA

Figure K-3a


HOT GAS
P-1501 & 02
CIRCULATION PUMPS
T-1101
HUMID. TOWER
HE-1303
WEAK ACID COOLERS
TK-1501
PUMP TANK
T-1102
WASH. TOWER
TO HOT COTTRELLS
EXIST. BUILDING LINE
NEW DAMPER
EXIST. BALLON FLUE
NEW DAMPER
REVERB. BOILER
REVERB. BOILER
REVERBERATORY FURNACE
JUG DAMPER
ESP
S-2802
ELECTROSTATIC ACID MIST PRECIPITATORS (ESP)(6)
ESP
HE-1302
HOT HEAT EXCHANGER
HE-1301
COLD HEAT EXCHANGER
EXISTING BUILDING LINE
S-2201
CONVERTER
HE-1304
CONDENSERS
DAMPER
HE-1310
GAS COOLER (2)
ST-2201
STACK
HE-1305
CONDENSERS
MOTOR CONTROL CENTER
T
M
CR-3101
REFRIGERATION UNIT
TK-1902
SEAL POT
HE-1308
SUPER-HEATER
TK-1904
PUMP TANK
B-1601A
M
MAIN GAS BLOWER'S ROOM
T-1104
TOWER
CT-1701
WATER COOLING TOWER
CW
CWR
HE-1307
ACID COOLER
TK-1903
PUMP TANK
M
B-1601B
HE-1306
ACID COOLER
ACID PUMPS
T-1103
DRYING TOWER
CONTROL ROOM

SCALE 1" = 40'-0"

PLOT PLAN OF REVERBERATORY GAS
SULFURIC ACID PLANT CASE II

TIM J. BROWDER COMPANY
Post Office Box 8473
San Marino, Calif. 91108, USA

Figure K-3b

costs is included here to provide a comparative review pointing out design/cost relationship.

Project construction schedule of 28 months is shown in Figure K-4. Capital costs vs. gas flow for various SO_2 concentrations is shown in Figure K-5. It can be expected that this 170,000 Nm^3/hr (100,000 SCFM) plant will cost approximately $22,000,000 and produce slightly less than 200 tons/day sulfuric acid.

Figure K-5 also shows comparable costs of conventional autothermal metallurgical single contact acid plants operating at 4% and 9% SO_2 gas. The trend in all cases is for costs to decrease as SO_2 concentration increases. Also the Browder system costs are considerably less than conventional single contact systems. The major reason for these cost variations is primarily because heat exchanger requirements are affected by the amount of energy available for heating the gas to the ignition temperature of 440°C (830°F). The Browder process provides a large LMTD thereby minimizing heat exchange surface area which can cost $15.00 per square foot.

K.9 ENERGY COMPARISON

The following results indicate the additional energy in terms of motor horse power and fuel oil required for Case I when compared to Case II. Additional details are given in Appendix K-1, page K-86.

	Connected	Average Operating
Electrically Driven Units		
Chilled Water Refrigeration Units	1,750 HP	1,625 HP
Preheater Blower	250 HP	235 HP
(Add to Case I)	2,000 HP	1,860 HP
Oil-Fired Preheater		
Fuel Oil	410 gal/hr	

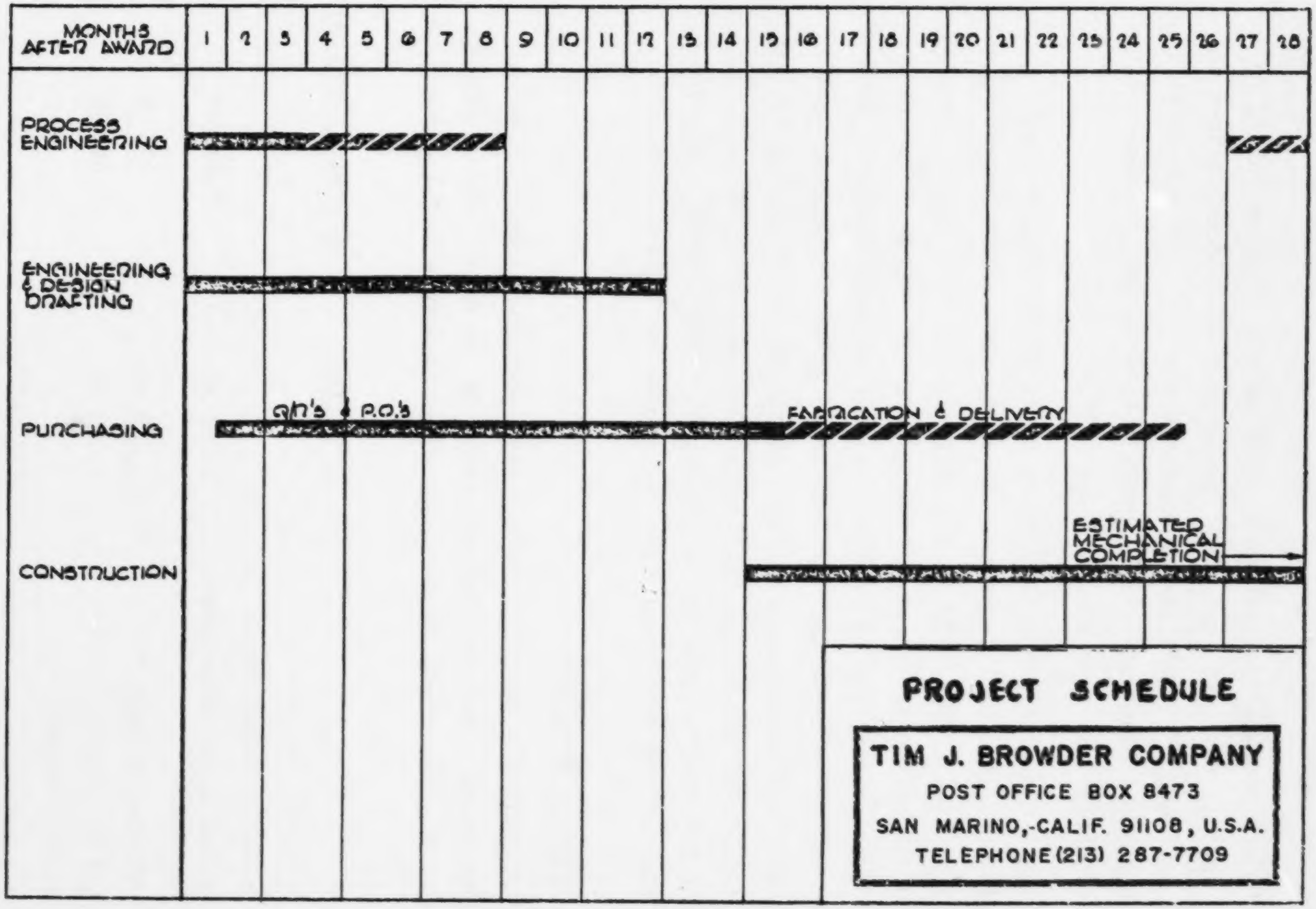


Figure K-4. Project Schedule

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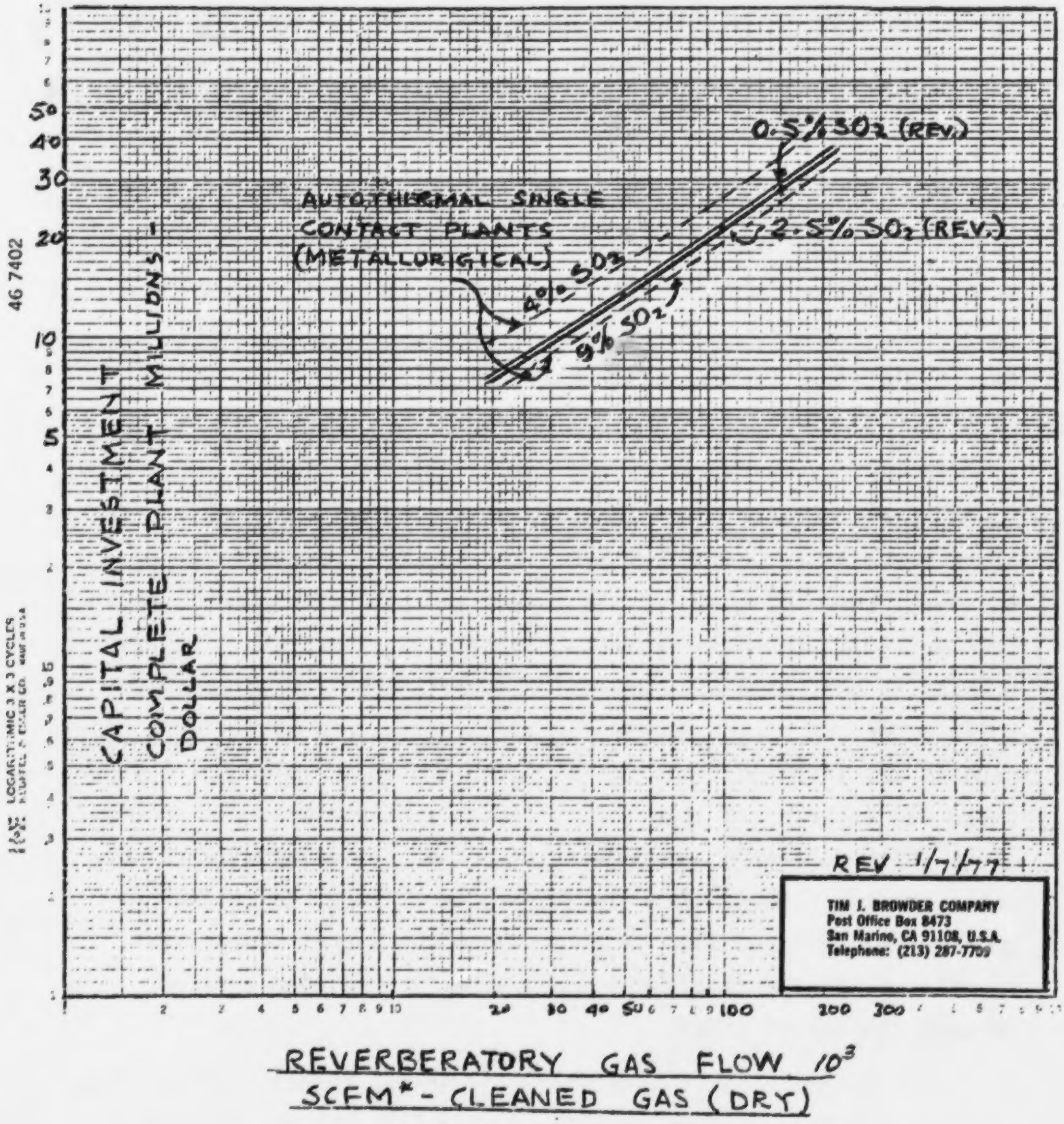
PLANT COST FOR REVERBERATORY FURNACE GAS SULFURIC ACID PLANTS
0.5 - 2.5% SO_2 - SINGLE CONTACT



TIM J. BROWDER COMPANY
Post Office Box 8473
San Marino, CA 91108, U.S.A.
Telephone: (213) 287-7709

* 32°F & 1 ATMOS

Figure K-5

APPENDIX L

LIME/LIMESTONE GYPSUM SO_2 CONTROL SYSTEM FOR REVERBERATORY FURNACE OFFGASES AT THE ONAHAMA COPPER SMELTER

The development of the lime/limestone gypsum SO_2 control system has been carried out over a period of approximately 20 years at the Hiroshima Technical Institute which is one of three R & D facilities operated by Mitsubishi in Japan.[60,61] Their work was initiated by reviewing scrubbing for all pollutants including particulates and SO_2.

As the main interest turned to SO_2 removal, attention was centered on the control of a sintering plant in the year 1957. Pilot plant tests at approximatley 3,000 Nm^3/hr were conducted for a period of three months. Pyrite sinter was used with ammonia as the feed materials to obtain ammonium sulfate as a product. The main problem at that time was converting ammonium sulfite to ammonium sulfate because of the demand for ammonium sulfate fertilizer. The process was intended to be installed at an industrial complex where there was an iron and steel plant within 6 kilometers of a chemical plant which made acid and fertilizer. A pipe line was planned between the two plants. This development work occurred during the period from 1957 to 1960. However, when the market dropped for fertilizer, the project was dropped after it had been carried through the design stage.

In 1962 pilot tests were conducted at the Kansai Electric Power Station at Amagasaki City near Osaka to select the absorbent and type of scrubber. The tests were conducted at the No. 3 power station which had an oil fired boiler with a gas flow of 5,400 Nm^3/hr (3,350 scfm). During this test program, ammonia, MgO, lime, limestone and red mud waste from an aluminum plant were considered as possible absorbents. Bayer process aluminum plants waste consisted of approximately 20 percent sodium along with aluminum, iron, titanium, silicon, and sulfur. Sodium aluminum silicate was obtained as a complex salt from the red mud by first separating out the iron oxide producing a white product. Using MgO to get sulfuric acid directly was not too successful because the best they could do at that time was to obtain 50 percent concentration.

It was determined, after the 1962 test program, that the lime/limestone system was the best because it was simple, the lime was readily available in Japan and the demand for gypsum was increasing. The requirement for gypsum in Japan is approximately one-third that of the U.S.

During the period between 1968 and 1972, the Hiroshima Technical Institute carried out a $5 million program to investigate the scaling problem which was occurring in the scrubber and the mist eliminator of the pilot plant lime/limestone system. The pilot tests carried out in 1962 had not uncovered this problem because of their relatively short duration, minimizing scale buildup. Fundamental research at the bench scale, as well as pilot scale of 2,000 Nm^3/hr (1,250 scfm), was included. Figure L-1 is a photograph of the pilot plant at the Hiroshima Technical Institute.

The sulfite scale was easy to remove but the sulfate was very hard. It was found that preparation and operating conditions of the absorbent were critical and required the proper range of pH, temperature, concentration, construction material of the scrubber, L/G, uniformity of the stream, and prevention of carry-over of mist to the eliminator. Their scaling work was reported at the EPA New Orleans meeting in 1971 including the development of the seed crystal technique.

Research and development work on a dry activated manganese oxide system during the period between 1964 and 1970 was also conducted. Pilot test work at the 1 MW, 55 MW and 110 MW levels was conducted. The 55 megawatt system was sponsored by MITI.

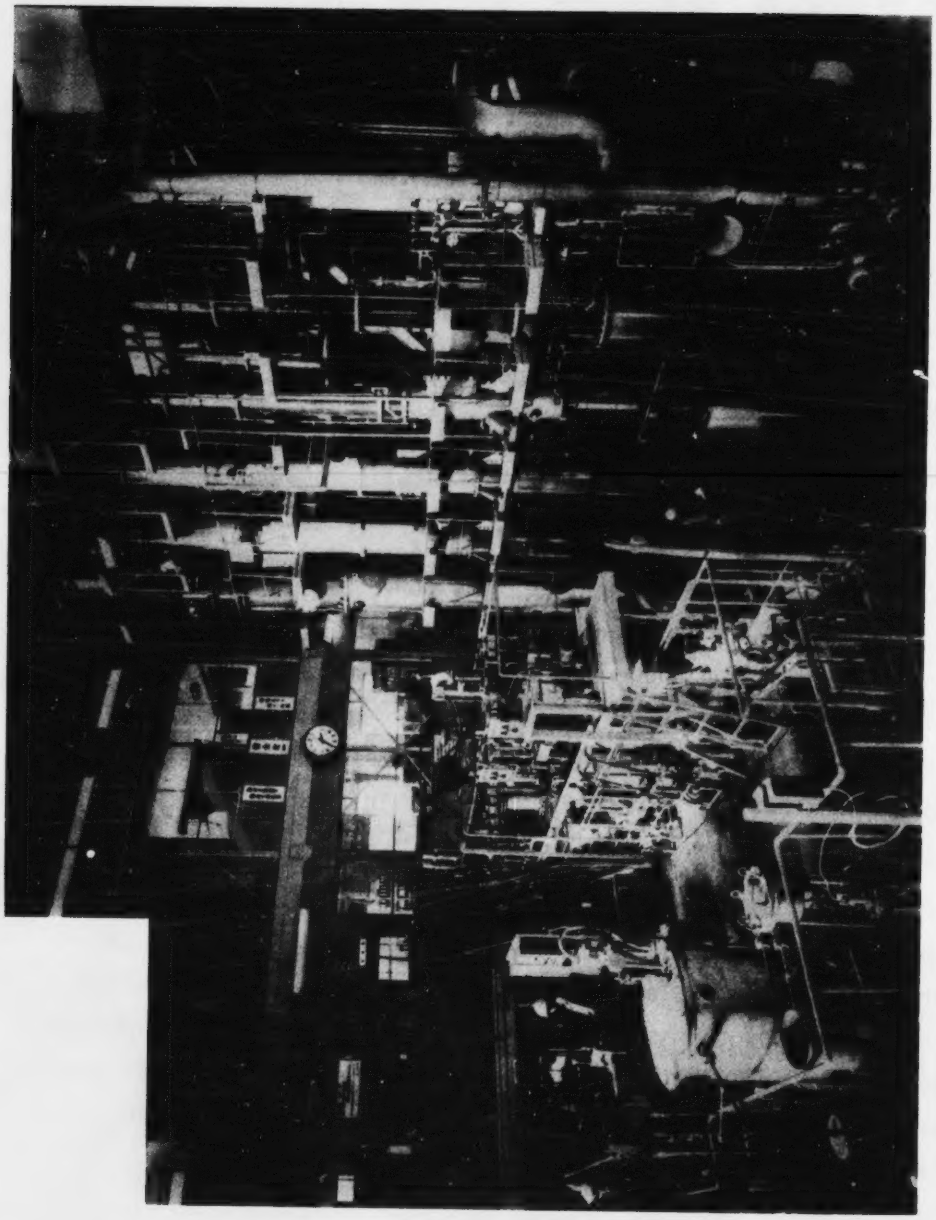


Figure L-1. Lime/Limestone Gypsum Pilot Plant

This work was then followed by a 220 megawatt installation at the Yokaichi Power Station on an oil fired system. The development was completed satisfactorily from a technical standpoint but did not go commercial because it was not economical.

Solid absorbents were also investigated. Handling the solid material absorbent was more difficult than the liquid, and it was also discovered that the wet system would take a higher SO_2 concentration. Furthermore, the byproduct was ammonium sulfate which is currently not being used very extensively in Japan as a fertilizer, having been replaced by urea. The solid or dry systems were reported at the 7th World Congress in Mexico City and also at the Los Angeles Chemical Engineering Society. at the present time Mitsubishi does not recommend dry systems particularly for reverberatory furnaces because the wet system can better handle the higher SO_2 concentrations even though the dry system does not require water or stack reheat. However, with the reverberatory furnace gases, it is not expected that large quantities of water will be required.

There was some bench scale testing at SO_2 concentrations of 20,000 ppm before the system for the Onahama smelter reverberatory furnace was constructed. However, no pilot plant work was done using the higher concentration compared to utility concentration.

APPENDIX M

COMPONENTS INCLUDED IN THE ONAHAMA LIME/LIMESTONE GYPSUM CONTROL SYSTEM

Washing Tower

The initial washing tower includes inlet ducting with internal sprays leading to a cylindrical vessel with a horizontal axis. Sprays are located along the top side. This unit is constructed of lead lined brick to provide resistance to corrosion from the low pH (1-2) water resulting from absorption of a slight amount of SO_2 and SO_3. Internal baffles are placed vertically to the axis at several intervals to cause mixing of the gas and spray by disturbing the flow pattern of the gas as it passes through the chamber. The gas leaving the washing tower is near saturation temperature. The pressure drop of this unit is approximately 70 mm H_2O.

Gas Coolers

The five gas coolers are sea water indirectly cooled heat exchangers.* These coolers drop the gypsum system inlet gas temperature in preparation from entry into the absorption towers. Cooling water required is 930 m^3/hour.

Absorption Towers

Two plastic grid packed absorbers in series are used. Their external shell is made of steel plates lined with synthetic rubber. The grid packing has large openings to minimize plugging and pressure drop.

The grid packed tower was adopted for the absorption units because its mass transfer coefficient for SO_2 absorption is high, its pressure loss low, the structure simple, its performance stability against load variation is large and in addition it can be scaled up or down easily.

---

*Ten coolers are commonly used when both the gypsum plant and the MgO plant are in operation.

The lower the pH of the absorbing solution the higher the Ca utilization. Conversely the lower the pH of the absorbing solution the higher will be the SO_2 concentration in the offgas. To lower SO_2 concentration at the outlet it is necessary to increase pH considerably. Therefore the rate of SO_2 absorption and Ca utilization can be satisfied only when a multistage absorber is used. The absorbers are designed so that the pH of the circulating solution in the #2 absorber is kept at 7, that of the absorbing solution to be taken out of #1 is decreased to 4 or less, which is also desirable for operation in the oxidizing section.

It is important to obtain an internal configuration producing an operating condition that prevents the slurry from stagnating and ensuring that all the inner surfaces of the absorber are sufficiently sprayed or covered with absorbing solution to avoid any pH variation which could occur locally which may provide a condition for scale generation. The addition of gypsum seed contributed to lowering of super saturated concentration of gypsum and makes a sacrificial surface to crystal precipitation. The piping systems are designed such that a suitable flow rate is maintained to prevent sedimentation of particles in the slurry as well as preventing clogging by installing strainers at suitable places.

Mist Eliminator

The mist eliminator located in the gas circuit downstream of the absorbers is of the Chevron type. It is internally coated with synthetic resin and made of steel.

Oxidizing Section

Three oxidizing towers are also internally coated with synthetic resin. Figure M-1 shows a schematic diagram of the rotary atomizers used to promote oxidation inside these towers. Absorbing solution taken out of the absorbing section is fed to the oxidizing tower where it is oxidized by air at pH 3.0 to 4.5 according to the follow equation:

$$CaSO_3.1/2\ H_2O + 1/2\ O_2 \xrightarrow[\text{Solution}]{\text{Aqueous}} CaSO_4.2H_2O$$

It is believed that the reaction of calcium sulfite advances through the medium of bisulfite ion. This reaction mechanism has also been proven by a correlation of the mass transfer coefficient of the oxidizing tower, pH value and bisulfite ion concentration.

The oxidation reaction depends on dissolution and diffusion of oxygen into the slurry. Decrease in air bubble diameter and increase in the amount of gas in the solution were the objectives of the rotary atomizer developed. Figure M-1 also shows the tower used for atomizer development. This atomizer tears with a shearing force caused by rotation between the surrounding solution and air layer. The air layer formed on the external surface of the cylinder which rotates at about 500 to 1000 rpm generates fine air bubbles of 0.1 to 1.0 mm.

The oxidizing towers are indirectly cooled with the cooling water going to a cooling tower for reuse in this circuit. The speed of oxidation is controlled by the pressure of the oxidizer. The oxidizer tower was designed for 70 psi and the actual nominal operating pressure of the air is between 40 and 45 psi (3 kg/cm^2).

Slurry Section

Slurry flowing out of the oxidizing tower is concentrated in a thickener. The underflow slurry from the thickener is treated by a basket type centrifugal separator to separate the dihydrate crystal of gypsum. The percentage of water content in the centrifuge material is 5 - 10 percent. Overflow liquid from the thickener and filtrate from the centrifuge is used for preparation of lime slurry and for other purposes.

Centrifuges

A vertical basket type centrifuge design is used. There are

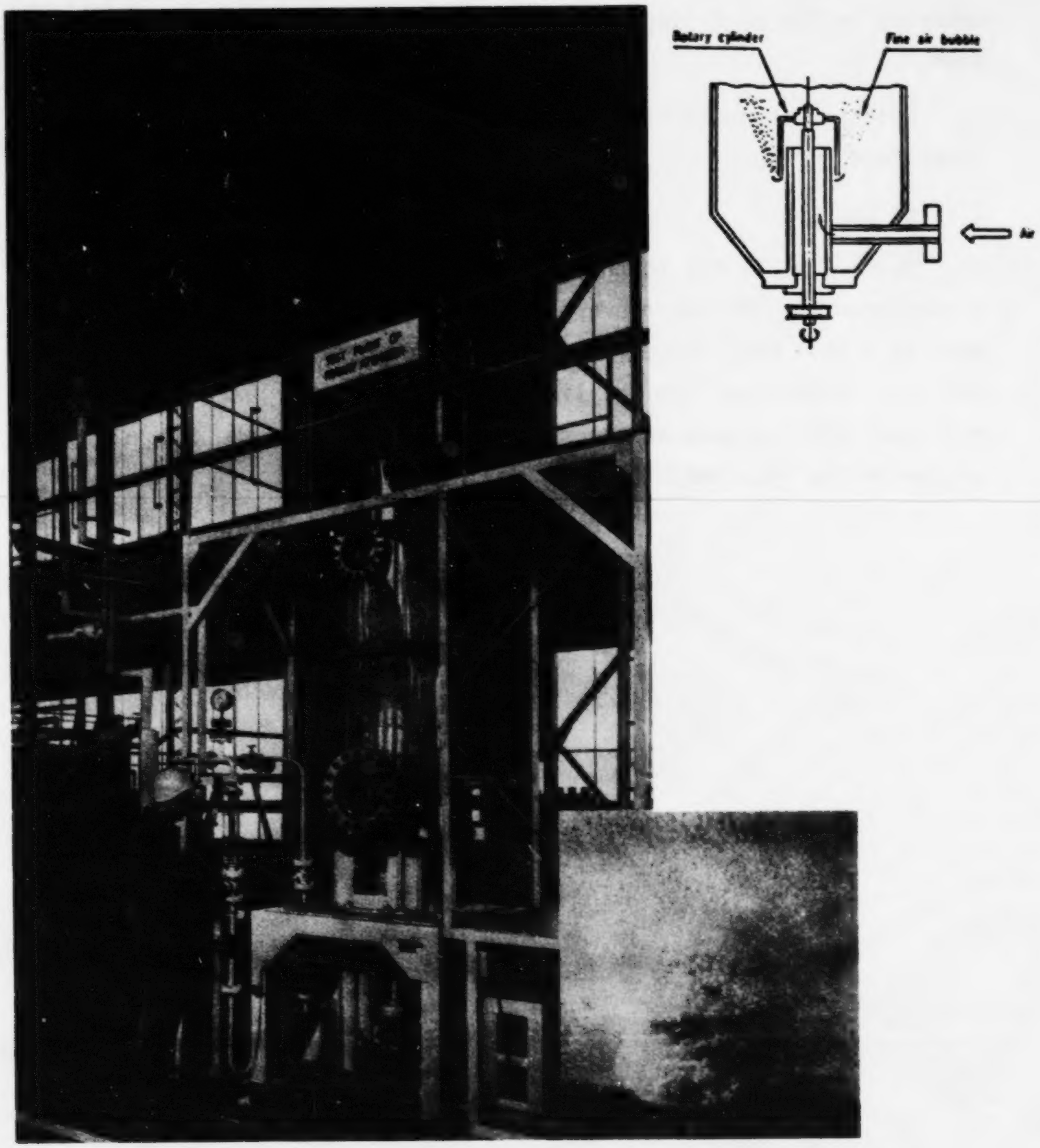

Rotary cylinder
Fine air bubble
Air

Figure M-1. Rotary Atomizer Schematic, Test Tower and Spray Pattern

14 centrifuges all operating continuously with no spares.

The smaller the crystal size the more difficult it is to separate in the centrifuge. Also small size tends to produce vibration.

Excessive amounts of silica in the gypsum tend to plug the centrifuge screens.

Slaking Section

Quick lime is fed to the slaker from a hopper and is mixed with liquid from the thickener overflow. From the slaker, the material goes to a ball mill where it is ground and passed through a liquid cyclone. Underflow from the liquid cyclone is recycled to the ball mill and overflow goes to the milk holder for use in the lime feed system to the absorber.

APPENDIX N

WATER BALANCE GYPSUM SYSTEM

This balance is for the lime-limestone-gypsum system being used at the Onahama copper smelter in Japan. Information received from the Onahama smelter indicated the water flowrates at different process locations. This information has been utilized to obtain an approximate water balance shown in Figure M-1.

Washing Tower and Gas Cooling Section

a) Quantity of water in flue gas

Flue gas rate at Onahama - 2,000 Nm^3/min = 70,600 SCFM

Amount of water in the flue gas = 0.116 lbs/lb of dry gas

Assuming the density of the flue gas

= 0.0808 lbs/ft^3 (Density of air)

$\therefore$Mass rate of flue gas = 0.0808 x 70,600

= 5,704 lbs/min

Quantity of water in the flue gas = 5,704 lbs/min

$$\times \frac{0.116 \text{ lbs } H_2O}{1.116 \text{ lbs gas}}$$

= 593 lbs/min

$\therefore$Quantity of dry gas = 5,704 = 593 = 5,111 lbs/min

b) Quantity of water in gas at outlet of Washing Tower

Assuming the gas is saturated with water vapor at the outlet of the washing tower and is at 60°C:

$$\text{Humidity ratio} = 0.623 \times \frac{\text{Partial Pressure of Water Vapor (Pv)}}{\text{Absolute Pressure of Vapor (Pa)}}$$

Pv at 60°C from steam tables = 2.890 lbs/sq in

Pa = 14.696 - 2.890 = 11.806 lbs/sq in

Humidity ratio = $0.623 \times \frac{2.890}{11.806} = 0.1525 \frac{\text{lbs } H_2O}{\text{lbs dry gas}}$

∴Water in gas at the outlet of the washing tower $= 5{,}111 \frac{\text{lbs dry gas}}{\text{min}} \times 0.1525 \frac{\text{lbs } H_2O}{\text{lbs dry gas}}$

∴Quantity of water added to flue gas in the washing tower = 785-593

= 192 lbs.

c) Quantity of water in gas at outlet of Gas Coolers

Quantity of dry gas = 5,111 lbs dry gas/min

Assuming the gas to be saturated at the outlet of the gas coolers and at 45°C:

Humidity ratio = $0.623 \frac{Pv}{Pa}$

$= 0.622 \times \frac{1.391}{13.305} = 0.0651 \frac{\text{lbs } H_2O}{\text{lbs dry gas}}$

∴Quantity of water in gas at the outlet of the gas coolers

= 5,111 x 0.0651

= 333 lbs of H_2O/min

d) Water balance

Therefore, in the Washing Tower and Gas Cooling System 785-332 = 453 lbs of H_2O/min is removed in the gas cooling system, whereas 192 lbs of H_2O/min is added in the washing tower.

Hence, in the Washing Tower and Gas Cooling Section, 260 lbs of H_2O/min excess water is removed from the flue gas and 324 lbs of H_2O/min remains in the gas to the Absorbers.

The Absorber Slurry System

Water Outlet Sources

a) Water going out to the ocean from the neutralization tank
= 6,636 lbs/min (4,336 M^3/day)

b) Some water is removed from the system by the mass of gypsum being produced by two processes; i) surface moisture, and, ii) water of crystallization.

Assuming the gypsum contains 10 percent surface moisture:

∴Water going out of the system as:

(i) surface moisture with gypsum = 450 x 0.1 = 45 TPD

= 62.5 lbs of H_2O/min

(ii) Mass of water of cyrstallization with gypsum can be obtained from the chemical formula of gypsum

Molecular weight of $CaSo_4 .2H_2O$ = 172.17
where molecular weight of $2H_2O$ = 36

∴Water of crystallization in gypsum = $\frac{36}{172.17}$ x (450 -45) TPD

= 84.7 TPD

= 118 lbs/min

∴Total mass of water in gypsum = 118 +62
= 180 lbs/min

c) The moisture in the exhaust gases through the main stack is another source of moisture loss.

Assuming the gas is saturated with water vapor at the outlet of the main stack and is at 45°C

∴The Humidity ratio = $0.623 \frac{Pv}{Pa}$

$= 0.622 \frac{1.391}{13.305} = \frac{0.0651 \text{ lbs } H_2O}{\text{lbs dry gas}}$

∴Quantity of water in gas at the outlet of the main stack

= 5,111 x 0.0651

= 333 lbs of H_2O/min

d) Total water outlet from system = 6,636 + 180 + 333

= 7,149 lb/min

Water Inlet Sources

a) Water in flue gas at inlet to Absorbers = 333 lbs/min

b) Water inlet due to pump seal leakage = 3,673 lbs/min (2,400 M^3/day)

c) Water from atomizer leaks = 459 lbs/min (300 M^3/day)

d) Water from TCA spill gas system = 1,613 lbs/min (1,054 M^3/day)

e) Water from Miscellaneous Sources being input to the neutralization tank:

= 1,071 lbs/min (700 m^3/day)

f) Total water inlet to system 7,149 lbs/min

∴Water inlet (7,149 lbs/min) = Water outlet (7,149 lbs/min)

APPENDIX O

MAGNESIUM OXIDE SYSTEM COMPONENT AND COST CONSIDERATIONS

The TCA absorber is 26.5 meters high and 4 meters in diameter. The rotary calciner is 52 meters long and 3.4 meters in diameter. Each of the two dryers used contains 900 sq. meters of steam drying surface area.

The blower is designed for 2200 m^3/minute at 900 KW. One spare blower is also available. The slaker is 35 m^3 and the ball mill is 2 meters by 4 meters.

The cost of operation of the MgO system is higher than the gypsum system but is still in the range of four to five cents per pound of copper, assuming no credit for product sales. The MgO system would have an advantage over the gypsum system in terms of the operating cost providing that there is an existing acid plant to treat the SO_2 gas from the MgO plant and the acid credit is reasonable. Capital costs of both systems are the same and presently considered to be $7,500,000 for the 1500 Nm^3/minute size system at Onahama.

APPENDIX P

CHEMISTRY INVOLVED IN MAGNESIUM OXIDE SYSTEM

The simplified chemical reactions taking place in the process may be written as follows:

Absorber:

$MgO + SO_2 + 3H_2O \longrightarrow MgSO_3 \cdot 3H_2O$ (very little formed)

$MgO + SO_2 + 6H_2O \longrightarrow MgSO_3 \cdot 6H_2O$

$MgSO_3 + \frac{1}{2}O_2 + 7H_2O \longrightarrow MgSO_4 \cdot 7H_2O$

Dryer:

$MgSO_3 \cdot 3H_2O \xrightarrow{heat} MgSO_3 + 3H_2O$

$MgSO_3 \cdot 6H_2O \xrightarrow{heat} MgSO_3 + 6H_2O$

$MgSO_4 \cdot 7H_2O \xrightarrow{heat} MgSO_4 + 7H_2O$

Calciner:

$MgSO_3 \xrightarrow{heat} MgO + SO_2$

$MgSO_4 + \frac{1}{2}C \xrightarrow{heat} MgO + SO_2 + \frac{1}{2}CO_2$

Input Material and Preparation

The magnesium hydroxide is purchased as a liquid containing

20-30 percent solids of $Mg(OH)_2$. Analysis of this material is:

CaO	0.97%
SO_4	0.30%
MgO	17.68%
H_2O	remainder

APPENDIX Q

WATER BALANCE IN THE MgO SYSTEM

Washing Tower and Gas Cooling Section

a) Flue gas

Flue gas flow rate = 1,500 Nm^3/min = 52,970 SCFM

Humidity ratio of flue gas = 0.116 lbs of H_2O/lb of dry gas

Density of flue gas = 0.0808 lbs/ft^3 (Density of air)

$$\therefore \text{Mass rate of flue gas} = 52{,}970 \text{ SCFM} \times 0.0808 \frac{\text{lbs}}{\text{ft}^3}$$

$$= 4{,}280 \text{ lbs/min}$$

∴Quantity of water in the flue gas

$$= 4{,}280 \text{ lbs/min} \times \frac{0.116 \text{ lbs } H_2O}{1{,}116 \text{ lbs wet gas}}$$

$$= 445.87 \text{ lbs/min}$$

$$\therefore \text{Quantity of dry gas} = 4{,}280 - 445$$

$$= 3{,}835 \text{ lbs/min}$$

b) Washing Tower

Assuming that the gas is saturated with water vapor at the outlet of the washing tower and is at 60°C

Humidity ratio of gas at outlet

$$= 0.622 \frac{Pv \text{ (Partial pressure of vapor)}}{Pa \text{ (Absolute partial pressure)}}$$

$$= 0.623 \times \frac{2.890}{11.806} = 0.1534 = .1525$$

∴Water in gas at the outlet of the washing tower

$$= 3{,}835 \times 0.1525 = 585 \text{ lbs } H_2O\text{/min}$$

∴Quantity of water added to the flue gas in the washing tower

= 585 -445 = 140 lbs/min

c) Gas coolers

Assuming that the gas is saturated with water vapor at the outlet of the gas coolers and is at 45°C:

Humidity ratio of gas at outlet of the gas coolers = 0.623 x 1.391/13.305

$$= 0.0651 \frac{\text{lbs } H_2O}{\text{lbs dry gas}}$$

∴The total quantity of water at exit of the gas coolers

$$= 0.0651 \frac{\text{lbs } H_2O}{\text{lbs dry gas}} \times 3{,}835 \text{ lbs/min}$$

= 250 lbs H_2O/min

d) Water balance

Water inlet to washing tower in flue gas = 445 lbs/min

Water outlet at gas coolers exit = 250 lbs/min

∴Total water lost by flue gas in the washing tower and gas cooling section is

= 445 -250 = 195 lbs/min

The Absorber Slurry System

a) Water in Make up Slurry

The composition of the make up slurry is given as follows:

CaO = 0.97% MgO = 17.68%

SO_4 = 0.3% H_2O = 81.05%

Also, quantity of Mg $(OH)_2$ being input is given: 1,128 lbs/hr
= 18.8 lbs/min

∴MgO being input = $18.8 \times \frac{40}{58}$ = 12.97 lbs/min

∴Quantity of H_2O in slurry = $12.97 \times \frac{81.05}{17.68}$

= 59.46 lbs/min

b) Water loss in dryer

To determine the quantity of water evaporated in the dryer, the following assumptions were made:

1. The cake going to the dryer is assumed to be $MgSO_3 \cdot 6H_2O$ since the MgO and $MgSO_4 \cdot 7H_2O$ in the cake are negligible compared to $MgSO_3 \cdot 6H_2O$.
2. The quantity of $MgSO_3 \cdot 6H_2O$ is calculated from the reaction between MgO and SO_2.
3. It is assumed that the cake contains 10% surface moisture.

$MgSO_3$ is formed in the absorber by the following reaction.

$$MgO + SO_2 \longrightarrow MgSO_3$$
$$40 + 64 \longrightarrow 104$$

It is also known that:

Volume flow of gas = 1,500 Nm^3/min

Volume flow of SO_2 = 1,500 x 0.026 = 39 Nm^3/min = 1,377 SCFM

$$\text{Density of } SO_2 = \frac{64 \text{ lb}_m\text{/lb-mole}}{359 \text{ ft}^3\text{/lb}_m\text{-mole}} \quad \frac{492°R}{520°R} = 0.16867 \text{ lb/ft}^3$$

$\therefore$ Mass flow of SO_2 = 1,377 scfm x 0.16867 lbs/ft^3 = 232.3 lbs/min

Ratio of $Mg(PH)_2$ makeup to SO_2 absorbed = 0.08 kg $Mg(OH)_2$/kg of SO_2

We know the quantity of SO_2 in the flue gas. Assuming 100% SO_2 absorption, quantity of MgO used is equal to:

$$\frac{232.3}{64} \times 40 = 145.2 \text{ lbs/min}$$

$$\therefore \text{Quantity of } MgSO_3 \text{ produced } \frac{145.2}{40} \times 104$$
$$= 377.5 \text{ lbs/min}$$

Amount of water of crystallization in $MgSO_3 \cdot 6H_2O$

$$= \frac{377.5}{104} \times 108 = 392.0 \text{ lbs/min}$$

∴Total amount of $MgSO_3 . 6H_2O$ produced = sum of $MgSO_3$ produced plus water of crystallization
= 377.5 +392.0 = 769.5 lbs/min

∴The total quantity of the cake going through the dryer
= 769.5/0.90 = 855.0 lbs/min

All the surface moisture and water of crystallization is driven off in the dryer

∴The quantity of water lost from the dryer

= 855.0 =377.5 = 477.5 lbs/min

c) Water Balance

The quantity of water coming into the system from the pump seals is given as 11 T/hr = 411 lbs/min.

The quantity of slurry purged = 10 T/day 15.6 lbs/min. Assuming 90 percent of the slurry purged is water, the quantity of water purged = 15.6 x 0.9 = 14.04 lbs/min.

∴Water coming into the system = water through the pump seals + water in makeup slurry = 411 + 59 = 470 lbs/min

Water coming out of the system = water lost from the dryer + water lost in the purged slurry = 477.5 + 14.04 = 492 lbs/min.

Note: the overall water balance indicates more water leaving the system than being charged to the system. The difference can be attributed to combustion products, miscellaneous sources of water of which data were not available and measurement errors.

APPENDIX R

PROCESS CHEMISTRY FOR THE CITRATE PROCESS[62]

Absorption of SO_2 in aqueous solution is pH dependent, increasing at higher pH. Dissolution of SO_2 forms bisulfite ion with resultant decrease in pH by the following reaction:

$$SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+$$

However, by incorporating a buffering agent in the solution to inhibit pH decrease, high SO_2 loading and substantially complete SO_2 removal from the waste gases can be attained. This citrate ion performs this buffering action by the following reaction:

$$H^+ + H_n\ Ci^{(3-n)} \rightleftharpoons H_{n+1}\ Ci^{(2-n)}$$

The chemistry for the production of sulfur and regeneration of absorbent by reacting H_2S with the SO_2 in the aqueous solution is complex, but the overall reaction is as follows:

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$$

Hydrogen sulfide for regenerating the absorbent and precipitating elemental sulfur can be produced by reacting sulfur with methane and steam by the following reaction:

$$CH_4 + 4S + 2H_2O \longrightarrow CO_2 + 4H_2S$$

APPENDIX S

PROCESS CHEMISTRY FOR FLAKT CITRATE PROCESS[63]

The chemical reactions in the absorption stripping operation follows the simplified reaction scheme given below.

$$SO_2\ (g) \rightleftarrows SO_2\ (aq) \qquad (1)$$

$$SO_2\ (aq) + H_2O \leftrightarrows H^+ + HSO^-_3 \qquad (2)$$

$$H^+ + H_n\ Ci^{(3-n)} \leftrightarrows H_{n+1}\ Ci^{(2-n)} \qquad (3)$$

Ci denotes the citrate ion, with n = 0, 1 or 2. The forward reactions take place during absorption, and the reverse reactions during stripping.

Absorption of SO_2 in aqueous solution is pH dependent, increasing at higher pH. Because dissolution of SO_2 forms bisulfite (HSO_3^-) ion with the resultant decrease in pH by the reaction 2, the absorption of SO_2 in aqueous solution is self-limiting. However, by incorporating a buffering agent in the solution to inhibit pH decreasd (remove the hydrogen ions formed in reaction 2), high SO_2 loadings and substantially complete SO_2 removal can be attained. In the citrate process this is accomplished by the buffering action of the various citrate species by the reaction 3.

The buffering capacity is naturally dependent on the concentration of citric acid and sodium hydroxide and the relation between them. In the Flakt-Boliden citrate process, the concentration of sodium hydroxide is between once and twice that of citric acid. (The relationship chosen is dependent upon the raw gas composition). In most cases this results in the absorbent pH of 4 to 5. [64]

APPENDIX T

PROCESS CHEMISTRY FOR THE COMMINCO AMMONIA SO_2 CONTROL SYSTEM

The process consists of absorbing the SO_2 from the flue gas in aqua ammonia, forming a solution that is essentially ammonium bisulfite according to the following relations:

$$2NH_4OH + SO_2 \longrightarrow (NH_4)_2SO_3 + H_2O$$

$$(NH_4)_2 SO_3 + SO_2 + H_2O \longrightarrow 2NH_4HSO_3$$

In addition to ammonium bisulfite, some ammonium sulfate is also formed primarily by the reaction:

$$(NH_4)_2SO_3 + 1/2\ O_2 \longrightarrow (NH_4)_2SO_4$$

Since the aim of the L.C. process is to make ammonium sulfate to be used as a fertilizer, the ammonium bisulfate combines with sulfuric acid to produce ammonium sulfate by the reaction:

$$2NH_4HSO_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + 2SO_2 + 2H_2O$$

$$(NH_4)_2SO_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + SO_2 + H_2O$$

APPENDIX U

PROCESS CHEMISTRY FOR WELLMAN-LORD SYSTEM[64]

The process is based on the chemistry of the sodium sulfite/bisulfite system. Flue gas containing SO_2 is scrubbed with a solution consisting of soluble Na_2SO_3, $NaHSO_3$, and Na_2SO_4. The SO_2 reacts with sodium sulfite to form sodium bisulfite according to the following reaction.

$$SO_2 + Na_2SO_3 + H_2O \longrightarrow 2\ NaHSO_3$$

In the regeneration cycle, the above reaction is reversed by the application of heat releasing sulfur dioxide and regenerating the sodium sulfite.

$$2\ NaHSO_3 \longrightarrow Na_2SO_3 + SO_2 + H_2O$$

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APPENDIX V

RECOVERY OF SULFUR FROM SMELTER GASES BY THE ORKLA PROCESS AT RIO TINTO

Submitted for discussion, 21st April, 1949.

Recovery of Sulphur from Smelter Gases by the Orkla Process at Rio Tinto[*]

By H. R. Potts[†], *Member*, and E. G. Lawford[‡], A.R.S.M., *Member*

Introduction

Numerous patents have been granted for processes designed to recover sulphur from industrial gases, but so far as the authors are aware only two or three of these processes have been successfully worked on a large scale; the object of this paper is to describe one that has given very successful results in at least three different countries—namely, the process which was worked out in Norway by Mr. N. E. Lenander of the Orkla Grube Aktiebolag and which has the distinguishing feature of recovering sulphur as a by-product of copper smelting.

Sulphur was first successfully recovered as a by-product from the blast-furnace smelting of pyritic copper ore at a small plant at Lokken, Norway, about the year 1928. The success of this pilot plant led to the construction of a large modern smelter with four blast-furnaces at Thamshaven, near Lokken, which was completed about 1932.

The first unit (a single blast-furnace) of the Rio Tinto plant went into production in August, 1930, and the plant has since been gradually expanded by the modification of two more furnaces of the original smelter, so that there are now, in all, three furnaces specially equipped for the recovery of sulphur.

Reference will, from time to time, be made to the plants of both the Orkla Company, Norway, and of Mina de S. Domingos, Portugal, operated by Mason & Barry, Ltd., but the main purpose of these notes is to describe the work at Rio Tinto, as the conditions are, in certain respects, markedly different from those prevailing at Orkla.

For convenience of presentation the paper is divided into three sections—namely, Section 1—Principles of the process; Section 2—The plant; Section 3—Practice of the process.

[*] Paper received on 12th January, 1949.

[†] Smelter superintendent, Rio Tinto Co., Ltd., 1934–1948.

[‡] Technical staff, Rio Tinto Co., Ltd.

SECTION 1—PRINCIPLES OF THE PROCESS

It will be remembered that in the smelting of pyritic copper ores the loose atom sulphur is distilled off at the top of the charge column and burns in atmospheric air. The iron monosulphide descends and at or near the focus burns in the oxygen of the blast, forming iron oxide (which is at once slagged) and sulphur dioxide gas; unoxidized monosulphide, together with the sulphide of copper, forms the matte, which also contains some magnetite and the sulphides of lead, zinc, etc. The authors have referred to the compound remaining after the distillation of the loose atom sulphur as monosulphide of iron, but actually this compound is generally considered to be Fe_nS_{n+1}, in which n is generally taken to be about 7. The reactions then are:

$$7FeS_2 = Fe_7S_8 + 3S_2 \quad \text{.......} \quad (1)$$

$$2Fe_7S_8 + 23O_2 = 14FeO + 16SO_2 \quad \text{.......} \quad (2)$$

It has long been realized that under certain conditions it is possible effectively to reduce SO_2 by solid carbon according to the equation—

$$SO_2 + C = CO_2 + \tfrac{1}{2}S_2 \quad \text{.......} \quad (3)$$

The inventor of the process therefore conceived the idea that if an ordinary blast-furnace, primarily designed for the smelting of sulphide ores to matte, could be fitted with a closed top very similar to that used on a conventional iron blast-furnace and that if, furthermore, a substantial excess of coke were added to the charge, two results would follow: First, the loose atom sulphur would not burn, as there would be no oxygen present and, secondly, the SO_2 produced at the focus would be reduced in the course of its ascent through the charge column, by the coke present. In this fashion a gas would be produced containing only nitrogen, carbon dioxide, and sulphur vapour, the last-named derived partly from the loose atom sulphur distilled from the pyrites while descending towards the focus, and partly from the reduction of the SO_2 formed near the focus. On cooling the gas the sulphur vapour would condense and the sulphur could thus be recovered.

The Norwegian experimenters found that it was quite a simple matter to close in the top of the furnace and to use for charging a line of bells similar to those used on an iron blast-furnace. They also found that when using 100 kg. coke per ton* of pyrites in the charge the effect was as expected and a substantial recovery of sulphur resulted.

Ideally, then, the aim of the process is to produce as much sulphur dioxide as possible at the focus and to have this travel up the column in such a way as to effect complete reduction by solid carbon before the gases leave the furnace. It is usually assumed that this reaction takes place for the most part in three stages.

*Th[illegible] out t[illegible] per t[illegible] tric t[illegible] 000 [illegible] 205 [illegible] used

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The first is represented by equation (3). In the second stage the CO_2 formed is reduced by coke a little higher up the furnace:

$CO_2 + C = 2CO$ .... (4)

The CO at once reacts with SO_2 thus:

$SO_2 + 2CO = \frac{1}{2}S_2 + 2CO_2$ .... (5)

This last reaction goes towards completion at temperatures below 600°C. It must be carefully noted that if equations (4) and (5) be added together and like molecules subtracted from each side of the equation the result is equation (3). Therefore, from the point of view of coke consumption per ton of SO_2 reduced, it matters not at all whether reduction proceeds in one step or in three, provided that all the CO involved is derived from CO_2 produced by equation (3) and not from other sources which will now be discussed.

Unfortunately the reduction of SO_2 by solid carbon—equation (3)—will only take place with reasonable rapidity at a temperature of about 1,200°C. and in the copper blast-furnace the high temperature zone does not extend for a sufficient distance above the focus to give efficient reduction. In other words, there is insufficient contact time at the temperatures prevailing for the coke to burn in SO_2 and much of it passes unburnt down to the focus, where it burns in oxygen to CO_2. The greater part of this CO_2 is reduced to CO just above the focus and then reduces SO_2 in accordance with equation (5). This burning of coke in air at the focus has two very ill effects: First, it means that reduction of SO_2 is done by CO, using 750 kg. of carbon per ton of sulphur instead of only 375 kg., the quantity required for reduction by solid carbon whether directly by equation (3) or in stages by equations (3), (4) and (5); secondly, the carbon consumes oxygen, which would otherwise be available for oxidizing FeS and producing SO_2. The practical manifestation of this effect is a large matte 'fall' of poor grade.

The fact has to be faced that, in attempting to carry out the reduction of sulphur dioxide by coke in a water-jacketed furnace within a few feet of the focus, the aim is to superimpose a reduction process on one which is essentially intensely oxidizing. The result is necessarily a compromise, in which the pyritic smelting is not very good and the reduction of sulphur dioxide somewhat inefficient.

A complete carbon and sulphur balance is set out in what follows and a quantitative analysis of the theory developed in an endeavour to assess the amount of SO_2 reduced by C and by CO respectively.

The authors must, however, state at the outset that in developing a quantitative analysis of the theory, they do so with great reserve, because of the enormous difficulties involved in obtaining accurate samples and analyses of the furnace gases; this subject deserves a paper to itself. Suffice it to say that even to-day it is not absolutely certain that the sampling and analysis at Rio Tinto gives the correct distribution of sulphur in the gases as between the various compounds SO_2, COS, CS_2, etc.

[illegible] in spite of this uncertainty and in spite of the

TABLE I

TYPICAL FURNACE FEED AND PRODUCTS
(in metric tons per furnace day)

	Tons	*Cu per cent*	*S per cent*	*Fe per cent*	*SiO_2 per cent*	*As per cent*	*Ash per cent*
FEED							
Pyrites.........	188·6	1·70	48·12	41·25	2·60	0·71	
Quartz	51·8			5·33	88·30		
Converter slag	23·0	2·75	1·60	55·53	18·00		
Limestone ...	16·6						
Sulphur	5·0		96·01			2·72	
Coke............	20·9						
Total	305·9						
PRODUCTS							
Matte	49·6	6·23	25·32	51·45			
Slag	101·6	0·36	2·54	40·78	33·30		
Dust............	1·5						
Crude sulphur	58·5		96·91			2·12	0·20

	Per cent by Vol.	*g. per cu. m.*	*g. per cu. m.*	
GASES			*C*	*S*
CO_2	13·8		73·98	
CO	0·9		4·82	
O_2................	0·5			
SO_2	3·0			42·7
H_2S	0·41			6·1
CS_2		24·34	3·84	20·5
COS		13·7	2·90	7·7
S		3·0		3·0
Total			85·54	80·0

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fact that they make certain broad assumptions the validity of which may possibly be questioned, the authors think it is worth while to set out a quantitative analysis of the reduction theory.

The data required are given in Table I.

The first step is the determination of the volume of gas per ton of pyrites smelted by means of the carbon balance.

	kg. of Carbon per 1,000 kg. pyrites
Charged to the furnace as coke	97·61
Carbon charged to furnace in limestone	9·32
Total carbon charged to furnace	106·93

Carbon in exit gases:

	g. Carbon per cu. m.
CO_2 13·8 per cent	73·98
CO 0·9 „ „	4·82
COS	2·90
CS_2	3·84
Total	85·54

Therefore the volume of gas per 1,000 kg. pyrites is—

$$\frac{106{\cdot}93 \times 1{,}000}{85{\cdot}54} = 1{,}250 \text{ cu. m.}$$

The total sulphur in the exit gases per 1,000 kg. pyrites will therefore be:

In SO_2	42·7	g. S per cu. m.	×	1,250	53·3 kg.
„ H_2S	6·1	„ „ „ „	×	„	7·7 „
„ CS	20·5	„ „ „ „	×	„	25·6 „
„ COS	7·7	„ „ „ „	×	„	9·6 „
„ S	3·0	„ „ „ „	×	„	3·8 „
Total	80·0	„ „ „ „	×	„	100·0 „

The sulphur balance can now be constructed as in Table II on page 433.

The first step in the quantitative analysis of the theory is to determine the quantities of sulphur produced respectively by the reduction of SO_2 and by the volatilization of volatile sulphur. The calculation follows:

	kg. S per 1,000 kg. pyrites
1. *Calculation of volatile sulphur*	
Total sulphur in pyrites	482·2
Less Sulphur combined with Cu, Pb, Zn, etc.	19·0
Sulphur in FeS_2	463·2
Therefore, volatile sulphur (42 per cent of sulphur in FeS_2)	194·5
Add Sulphur in residues	25·4
Total volatile sulphur	219·9

2. *Calculation of sulphur recovered by reduction of SO_2*

		kg. S per 1,000 kg. pyrites
Total sulphur charged to furnace		509·6
Deduct volatile sulphur, volatilized		219·9
Fixed sulphur entering smelting zone as Fe_7S_8 and non-ferrous metal sulphides		289·7
Deduct Sulphur in matte	66·5 kg.	
Slag	21·5 ,,	
Dust	1·6 ,,	
		89·6
Therefore, sulphur oxidized by blast to SO_2		200·1
Sulphur lost in gases and unaccounted		119·5
Balance, sulphur recovered by reduction of SO_2		80·6

The sulphur lost in gases as S, CS_2, H_2S and COS must also at some stage have existed as elemental sulphur. It does not matter whether this sulphur is assumed to come from volatile sulphur or from SO_2 because if its origin is the volatile sulphur then more than 80·6 kg. sulphur must have been reduced from SO_2. Thus we have :

	kg.	*kg.*
Sulphur produced by reduction of SO_2		80·6
Sulphur produced by reduction of SO_2 but subsequently reacted to form CS_2, COS, H_2S—		
CS_2	25·6	
COS	9·6	
H_2S	7·7	
	42·9	
Elemental S	3·8	
		46·7
TOTAL S formed by reduction of SO_2		127·3

The carbon entering into the reduction reaction is the total carbon charged to the furnace, 97·61 kg., less the carbon combined to form CS_2, COS and CO, 14·5 kg. Thus the carbon entering the reaction is 83·11 kg.

Of the carbon reaching the focus and burning to CO_2 not all will be reduced to CO. It has been assumed that some 10 per cent will not be reduced and will pass into the gases as CO_2.

With the above data and assumptions it is now possible to calculate what proportion of the total sulphur reduced from SO_2 is reduced by CO and by solid C.

Let x = weight of carbon reducing SO_2 by equation (3).
y = weight of carbon burnt to CO_2 at the focus but subsequently reduced to CO and which then reacts with SO_2 by equation (5).

$$x + y = 83{\cdot}1$$

$$32x + \frac{32}{}(y - \frac{0{\cdot}1y)}{} = 127{\cdot}3$$

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TABLE II

	Tons	*Per cent S*	*Sulphur tons*	*kg. S per 1,000 kg. pyrites*
CHARGED TO FURNACE				
Pyrites	188·0	48·12	90·7	482·2
Residues	5·0	96·91	4·8	25·4
Converter slag	23·0	1·60	0·4	2·0
Quartz	51·8	—	—	—
Limestone	16·6	—	—	—
TOTAL	285·0	—	95·9	509·6
Coke	20·9	—	—	—
PRODUCED				
Crude sulphur	58·5	96·91	56·6	300·5
Matte	49·6	25·32	12·6	66·5
Slag	161·6	2·54	4·1	21·5
Dust	1·5	18·0	0·3	1·6
Gases	—	—	18·6	100·0
Unaccounted loss	—	—	3·7	19·5
TOTAL	—	—	95·9	509·6

Solving this equation gives $x=18{\cdot}8$ and $y=64{\cdot}3$. Thus the sulphur reduced by CO is 77·3 kg. and the sulphur produced by reaction of SO_2 with solid C is only 50 kg. or less than 40 per cent of the total.

In the Appendix the figures for the three years 1936, 1937, and 1938 have been consolidated and the calculation of the amount of sulphur produced by reduction by C and CO respectively has been made. It shows a widely different result and it must be concluded that no precise quantitative evidence can be produced. All that can be said is that a considerable proportion of the total sulphur recovered by the reduction of SO_2 is produced by CO at a carbon consumption of 750 kg. per ton sulphur and that the proportion produced by the efficient reduction by solid C at 325 kg. carbon per ton sulphur is probably always less than 66 per cent.

As the exit gases contain a substantial amount of unreduced O_2 it [illegible] be [illegible] ght [illegible] incre[illegible] the [illegible] m/p[illegible] ratii.e., adding more coke to the charge—would effect a greater degree of reduction and thus increase the recovery of sulphur. In practice, however, although it is possible that the amount of reduction is increased, there is no improvement in recovery for any increase in carbon beyond about 80 kg. per ton. The total sulphur in the gases remains the same, but with a different distribution between the various compounds ; SO_2 is diminished, but CS_2 and COS are increased.

It would seem in fact that the CS_2 and COS in the exit gases from the furnace are dependent on the amount of coke present, the concentration of the sulphur vapour and the quantity of CO in the gases. For example, the COS is formed by the action of CO on sulphur vapour at temperatures below 800°C., whereas CS_2 is formed nearer the focus by reaction between sulphur and hot carbon. The hydrogen sulphide in the gases depends very much upon the amount of sulphur dioxide in the exit gases and the concentration of water vapour present, a small reduction in the amount of sulphur dioxide present increases the H_2S, the increase being roughly in the proportion of $\frac{1}{\sqrt{\text{partial pressure}}}$ of SO_2 for any given concentration of water vapour.

The effects of varying the carbon/pyrites ratio (i.e. the percentage of coke on the burden) is shown in Table III. From these figures it will be seen that with 61 kg. of carbon per ton the process evidently suffers from a deficiency of reducing agent. The SO_2 is very high and the other sulphur compounds are not markedly low. On the other hand, with 104 kg. carbon there is no decrease in the total sulphur lost although there is much less SO_2, as compared with Gas 2 (Table III).

TABLE III

	1	2	3
Carbon charged per ton pyrite, kg.	104·0	77·3	61·0
Sulphur as SO_2 g./cu. m.	39·2	51·6	70·8
,, ,, CS_2 ,, ...	18·6	5·0	5·8
,, ,, COS	7·0	6·2	4·8
,, ,, H_2S	6·9	7·3	4·6
Total sulphur	71·7	71·0	86·0
CO_2 Vol. per cent	14·3	12·6	11·0
CO ,, ,, ,, ...	0·8	0·5	0·6
O_2 ,, ,, ,, ...	0·5	1·0	0·8

The conclusion is, therefore, that, where conditions make impossible the further treatment of the exit gases, the most

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economical percentage of coke on pyrite will correspond to about 80–90 kg. carbon per ton of ore. Where, however, gases are free of arsenic and can be subjected to catalysis after they leave the furnace, the coke can be profitably increased because the catalysing of Gas 1 (Table III) will yield a total of 34 g. sulphur per cu. m., whereas the catalysis of Gas 2 would only yield 21 g. per cu. m. In other words, with 1,250 cu. m. gas per ton pyrites, the extra 27 kg. of carbon would produce an additional 16 kg. of sulphur.

The reactions upon which catalysis of the exit gases depends are:

$$SO_2+CS_2 = CO_2 + \tfrac{3}{2}S_2 \quad \dots\dots \quad (6)$$

$$SO_2+2COS = 2CO_2 + \tfrac{3}{2}S_2 \quad \dots\dots \quad (7)$$

$$SO_2+2H_2S = 2H_2O + \tfrac{3}{2}S_2 \quad \dots\dots \quad (8)$$

At Orkla catalysis of the exit gases has always been most successfully practised and has resulted in a much higher overall recovery of sulphur than has so far been possible when treating the arsenical Iberian ores. The precise effect of arsenic is discussed later.

The type of smelting done in the Orkla process is pyritic, as it is the oxidation of a sulphide ore, and nearly 70 per cent of the heat generated is derived from the oxidation of iron sulphide. For the process to work well and smoothly it is essential that a high rate of oxidation should be at all times maintained and to ensure this a flux containing a high percentage of free silica is essential.

From what has been written it can be inferred that the conventional type of water-jacketed copper blast-furnace may not be the most suitable apparatus in which to carry out this process, in which a reaction zone has to be maintained at over 1,200°C. if the sulphur dioxide is to be reduced in the contact time available. This unsuitability has been recognized for a long time, but so far the problem of reconciling copper smelting with high sulphur recovery in one apparatus has not, in the opinion of the authors, been fully solved.

Notwithstanding all its admitted shortcomings, the Orkla process uses much less coke per ton of sulphur produced than any of the other reduction processes. The reason, of course, is that about 65 per cent of the sulphur recovered is the loose atom sulphur and only 35 per cent is derived from the reduction of SO_2, whereas all other processes first burn the raw material to SO_2. Thus at Rio Tinto slightly over 3 kg. crude sulphur per kg. of carbon is obtained, whereas the theoretical equivalent when reducing SO_2 by C is 2·66; in practice the figure is almost certainly less than 2·00 kg. crude sulphur per kg. of carbon.

The comparative inefficiency of SO_2 reduction in the Orkla furnace is therefore much less important from the economic standpoint than would be the case if all the sulphides in the feed to the furnace had first to be oxidized to SO_2. This point has an important bearing on the treatment of sulphides other than FeS_2.

SULPHUR PURIFICATION

The crude sulphur coming from the condensers and mist Cottrells contains 1·5–2 per cent of arsenic and 0·2–0·3 per cent of ash.

Arsenic is removed by circulating milk of lime through the molten sulphur in autoclaves. When the original experiments were carried out to determine the most efficient method of refining, various soda compounds were tried, with the idea of forming sodium thio-arsenate. It was found that when caustic soda was used mixed with lime a much quicker removal of arsenic resulted, but NaOH always gave the sulphur a peculiar greasy appearance and a bad colour. Finally, quick lime was decided upon as the best, cheapest, and most readily-available reagent. This removes arsenic very efficiently, provided the lime is of good quality and correctly used. The lime suspension is pumped through the sulphur and re-acts in the course of its passage with the arsenic present to form complex calcium thio-arsenates, the lime containing them being eventually run to waste. The arsenic in the crude sulphur is present as arsenic pentasulphide, As_2S_5, and the reactions which take place when the crude sulphur is scrubbed with a lime suspension are somewhat obscure, but it seems probable that the reaction between the quick lime and the arsenic sulphide in the crude sulphur proceeds by the formation of calcium thio-arsenate. As H_2S is not produced during refining the authors consider the reaction to be—

$$4\,Ca(OH)_2 + As_2S_5 + 2S_2 = Ca_3As_2S_8 + CaSO_4 + 4H_2O \quad \ldots\ldots\ldots \quad (9)$$

The theoretical requirement is thus 1·47 tons CaO per ton arsenic. It will be seen from Table IV that the actual consumption is between 1·8 and 2·2 tons free CaO per ton arsenic. There is always a portion of the CaO which fails to react because it is inert through being overburnt, also calcium polysulphides are formed. The treated sulphur contains some 8 to 10 parts per million of arsenic and is passed through ordinary steam-heated filter presses, these filters removing the ash so that the final product is sulphur of high purity.

SECTION 2—THE PLANT

The process flow-sheet is comparatively simple (Fig. 109), and various sections of the plant will be described in some detail before proceeding to the discussion of metallurgical results.

Before describing the individual units of the plant, a very brief summary of the sequence of operations will be given.

Sulphur-bearing gases from blast-furnaces are cleaned by passing through Cottrell electrostatic precipitator units; they then pass first through condensers, where the larger part of the sulphur is recovered, and then through a second set of Cottrells, where a further recovery of sulphur is made. The crude sulphur contains arsenic, which is removed by a washing process employing quick lime.

It should be clearly understood that the Rio Tinto plant is very much an improvization and that it certainly cannot be described as an ideal Orkla process layout. In this respect the Norwegian plants and that of Mina de S. Domingos, Portugal, are both much

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superior and it is hoped that a full description will be given during the discussion of this paper. The operators referred to had the advantage of being unencumbered with an existing copper smelter and so were able to build from the foundations with the Orkla smelting system in view. At Rio Tinto, on the other hand, there was already a smelter many years old and in many respects already antiquated, but from which the flow of copper had to be maintained. It was, therefore, necessary to create an Orkla smelting plant by a step-by-step modification of existing blast-furnaces, together with the addition of dust precipitators, sulphur condensers, etc., not in

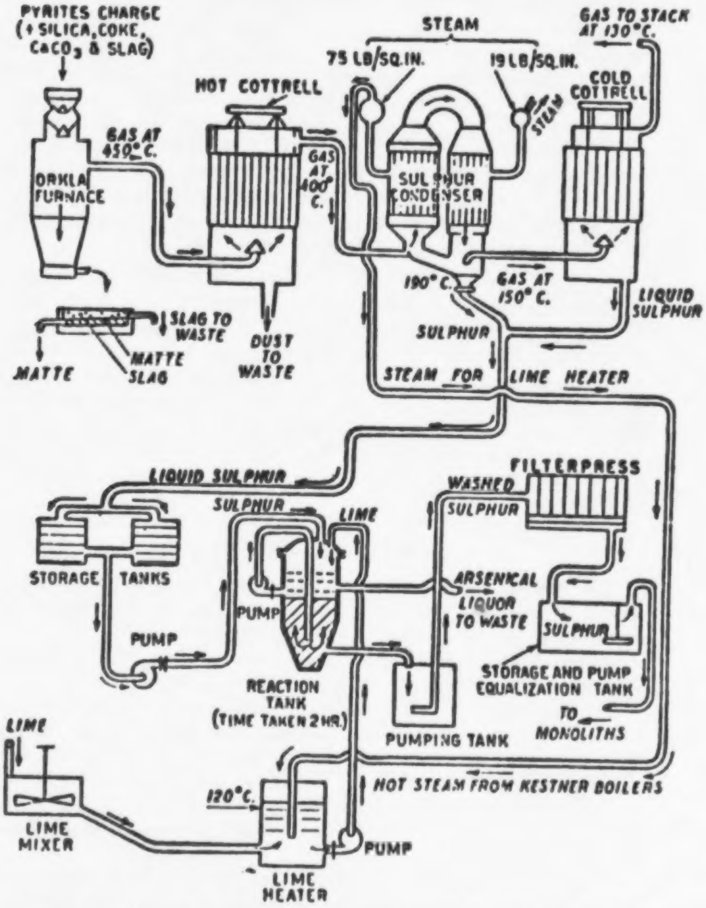
PYRITES CHARGE (+ SILICA, COKE, CaCO₃ & SLAG)
STEAM
GAS TO STACK AT 130°C.
75 LB/SQ.IN.
19 LB/SQ.IN.
HOT COTTRELL
COLD COTTRELL
STEAM
GAS AT 450°C.
ORKLA FURNACE
GAS AT 400°C.
SULPHUR CONDENSER
190°C.
GAS AT 150°C.
LIQUID SULPHUR
SLAG TO WASTE
DUST TO WASTE
SULPHUR
MATTE
MATTE
SLAG
STEAM FOR LIME HEATER
LIQUID SULPHUR
FILTERPRESS
WASHED SULPHUR
SULPHUR
LIME
STORAGE TANKS
PUMP
ARSENICAL LIQUOR TO WASTE
SULPHUR
PUMP
STORAGE AND PUMP EQUALIZATION TANK
REACTION TANK (TIME TAKEN 2HR.)
TO MONOLITHS
LIME
PUMPING TANK
HOT STEAM FROM KESTNER BOILERS
120°C.
LIME MIXER
PUMP
LIME HEATER

Fig. 109.—Flow-sheet—Orkla furnace and sulphur washing plant.

TABLE IV

ORKLA PROCESS OPERATING RESULTS

SMELTING	*Years 1940–1946 inclusive 3,721 furnace days*					*Years 1934–1939 inclusive 2,928 furnace days*				
	Metric tons	*Sulphur*		*Copper*		*Metric tons*	*Sulphur*		*Copper*	
		Per cent S	*Tons*	*Per cent Cu*	*Tons*		*Per cent S*	*Tons*	*Per cent Cu*	*Tons*
CHARGE										
Pyrites	634,345	46·80	297,112	1·90	12,050	535,832	46·80	251,255	3·57	19,139
Concentrates	5,285	35·60	1,886	12·80	653	—	—	—	—	—
Precipitate	—	—	—	—	—	69	—	—	69·50	48
TOTAL PRIMARIES	639,630	—	298,998	—	12,703	535,901	—	251,255	—	19,187
Washing plant residues	18,707	85·40	15,927	—	—	12,885	86·90	11,117	—	—
Clean up	2,566	85·00	—	—	—	779	—	—	—	—
Converter slag	58,413	1·51	879	5·21	3,047	59,764	1·75	1,040	4·76	2,848
Matte	9,627	23·6	2,270	9·08	874	7,692	24·60	1,897	16·25	1,246
TOTAL SECONDARIES	89,313	—	19,076	—	3,921	81,120	—	14,054	—	4,094
Silica flux	177,574	—	—	—	—	137,609	—	—	—	—
Limestone	48,276	—	—	—	—	47,332	—	—	—	—
BURDEN	954,793	—	318,074	—	16,624	801,962	—	263,309	—	23,281
Coke	57,638	—	—	—	—	55,816	—	—	—	—
Per cent on ore and concentrates	9·04%	—	—	—	—	10·4%	—	—	—	—
Per cent on burden	6·05%	—	—	—	—	6·9%	—	—	—	—

PRODUCTS										
Crude sulphur	188,433	97·2	183,828	—	—	167,319	97·3	162,740	—	—
Matte	165,248	23·7	39,113	9·55	14,150	135,694	25·1	34,149	14·80	20,178
Slag	535,920	2·92	15,661	0·327	1,755	444,536	2·66	11,823	0·385	1,703
Cottrell dust	5,189	21·21	1,110	1·96	96	3,373	19·40	655	1·84	61
Gases	—	—	69,560	—	—	—	—	50,240	—	—
Unaccounted	—	—	8,802	—	623	—	—	5,702	—	1,339
TOTAL	—	—	318,074	—	16,624	—	—	265,309	—	23,281
PURIFICATION				*Per cent As*	*As tons*				*Per cent As*	*As tons*
CHARGE										
Crude sulphur	188,145	97·2	183,646	2·02	3,696	166,685	97·3	162,299	2·21	3,664
Lime	8,127	—	—	—	—	6,644	—	—	—	—
PRODUCTS										
Sulphur	153,088	99·9	153,087	*Parts/10^6* 24	—	133,360	99·9	133,360	*Parts/10^6* 6	—
Waste liquor, m^3	80,263	*kg./m^3* 119·0	9,517	*kg./m^3* 49·5	3,949	90,253	*kg./m^3* 102·0	9,184	*kg./m^3* 41·5	3,740
Residues	19,150	85·10	16,356	—	—	12,881	87·1	11,222	—	—
Process loss	—	—	4,686	—	—	—	—	8,533	—	—

Of the 318,074 and 265,309 tons of sulphur entering the furnaces in the two periods, 15,927 and 11,117 tons of sulphur are from residues—that is, residues produced when refining sulphur which do not represent fresh sulphur entering the process.

The new sulphur is only obtained from the pyrites and concentrates and perhaps from the converter slag and matte.

If we assume the sulphur is coming from the above-mentioned four materials only, the sulphur recovery is:

1940–1946 $\frac{153{,}087}{(318{,}074-15{,}927)}$ = 50·66 per cent.

1934–1939 $\frac{133{,}360}{(265{,}309-11{,}117)}$ = 52·46 per cent.

If, however, we assume the sulphur recovered only comes from the pyrites and concentrates, then the sulphur recovery is:

1940–1946 $\frac{153{,}087}{(318{,}074-19{,}076)}$ = 51·2 per cent.

1934–1939 $\frac{133{,}360}{(265{,}309-14{,}054)}$ = 53·07 per cent.

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ideal sites and properly connected to the furnaces but on sites dictated by the availability of space in the existing plant.

There is no doubt that the ideal layout consists of smelting furnaces each coupled to its own dust precipitator and sulphur condenser, all precipitators and condensers being placed as close as possible to the furnaces. It will be seen from the description which follows how very far it has been necessary in the present case to depart from this ideal.

BLAST-FURNACES

Three out of the original six open-topped furnaces have been modified to allow sulphur recovery ; the first being No. 6 furnace, the most easterly one and, therefore, nearest to the hot Cottrells. The conversion of Nos. 5 and 4 furnaces followed later. The dates upon which these three furnaces were first blown in after being modified were : No. 6, 1 Aug. 1930 ; No. 5, 5 Sept. 1932 ; No. 4, 10 Feb. 1942.

The normal copper-smelting furnace is preserved in its usual form up to the level of the charging floor, but instead of the top being left open and charging effected through side doors on the level of the charging floors, the top was heightened, completely closed in, and equipped with four sets of double-valved charging bells, very similar to the gas-tight bells used on the normal iron blast-furnace ; by this means charge can be introduced into the furnace without allowing any access of atmospheric air. Fig. 110 (Plate XXI) shows the construction.

It will be seen from Table V that the dimensions of the three furnaces are not identical. All of them have the same height and use standard 12-ft. side jackets, but the rake of the jackets is different, being much greater in No. 6 ; this large flare was originally given with the idea of reducing the gas speeds in the furnace and thereby effecting a better reduction of SO_2 ; the authors think that in many ways No. 6 has been consistently the most satisfactory furnace, perhaps because, having the shortest flue connecting it with the hot Cottrells, less back pressure is developed and a faster smelting rate results. However, the wide flare has the disadvantage of needing specially large, non-standard end and breast jackets. The jackets are all made entirely by electric welding, the fire sheets being of a $\frac{3}{8}$-in. mild steel, and the back sheets of $\frac{5}{16}$-in. The 12-ft. jackets are satisfactory on the open-topped furnaces, but they are not sufficiently stiff to resist the heavy thrust imposed by an 18-ft. charge column and they tend to buckle, even though they are reinforced by three heavy buck stays bolted across each side of the furnace. Leading particulars are given in Table V.

The upper part of all the furnaces, above the jackets, is supported on a framework of box girders and consists of a steel box welded at the joints. This is solidly lined with 18 in. of good-quality firebrick ; the roof of the furnace between the charging bells is formed by an arch made of carefully cut and fitted firebricks. The furnace

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TABLE V

	No. 6 Furnace	*Nos. 4 and 5 Furnaces*
Length	18 ft.	18 ft.
Number of charging bells	4	4
Height from closed bells to floor	21 ft. 7 in.	22 ft.
Height from top of jackets to roof	10 ft. 2 in.	9 ft. 11 in.
Width at top of jackets	9 ft. 4 in.	5 ft. 5 in.
„ „ tuyères	4 ft. 5 in.	3 ft. 5 in.
Hearth area	82·6 sq. ft.	61 sq. ft.
Number of tuyères	36	36
Diameter of tuyères	4 in.	4 in.
Tuyère area	3·14 sq. ft.	3·14 sq. ft.
Ratio—Hearth to tuyère area	26 to 1	19 to 1
Height c/l of tuyères to floor	2 ft. 6 in.	2 ft. 6 in.
Number of gas ports	5	18
Height of gas ports	1 ft. 6 in.	1 ft. 4 in.
Width of gas ports	3 ft.	7½ in.
Total area of gas ports	22·5 sq. ft.	14·4 sq. ft.
Number of side jackets	12	12
Dimensions of side jackets	12 ft. 3¾ in. by 3 ft.	12 ft. 3¾ in. by 3 ft.
Flare of jackets from centre line of tuyères	1 ft. in 2 ft.	1 ft. in 4 ft. 9 in.

bottom is put in with one lower row of firebrick and an upper one of magnesite brick; the use of firebrick alone for the furnace bottoms has been found unsatisfactory, because of the scouring effect of the slag.

The practice of lining the inner side of the water jackets completely with good-grade firebricks for the full height of the jacket, has been made standard in the Norwegian plants, upon the supposition that this will maintain a higher temperature next to the jacket and therefore lead to better reduction of SO_2, and also that the hot surface of the brickwork may have a catalysing effect. This lining has been tried once or twice at Rio Tinto, but its use has been discontinued for many years past, as it was found that the lining is soon fluxed away, leaving the jackets bare again.

The gases leave the top of the furnaces through ports and are conducted to the hot Cottrells by rectangular insulated flues, which lead into a junction box, on which the valves for regulating the flow of gas into the various filter chambers are situated, each pair of chambers having its own isolating valve.

The flues connecting Nos. 4 and 5 furnaces have each an internal cross-sectional area of 14·30 sq. ft.; the flues are well insulated with 1¼-in. thick slabs of an asbestos material, backed up by a firebrick lining; the calculated gas speed through these flues at 400°C. is 17·5 ft./sec. These long flues are an undesirable feature of the Rio Tinto plant, but because of the existing layout of the original furnace plant they are unavoidable. They form a great obstacle on the furnace feed floor, hindering ready access to the furnaces; they also slowly fill up with a layered deposit of dust

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APPENDIX W

FW-BF DRY ADSORPTION SYSTEM[66,67]

W.1 HISTORY

A 20 MW demonstration FW-BF dry adsorption system was put into operations at the Scholz Steam Plant of Gulf Power Company near Sneads, Florida by Foster Wheeler Energy Corporation in 1975. The technical basis for this system is derived from a license with Bergbau-Forschung GmbH, the research group for the German Bituminous coal industry. The basis of design for both the Gulf Power Demonstration Unit and the STEAG Demonstration Unit at Lunen, West Germany, is the very extensive work done by Bergbau-Forschung over a two year period at their pilot unit at Welheim, Germany. This plant ran for one continuous period of 6,000 hours, and the results of the two year testing period were published in 1970 at the Second International Clean Air Congress in Washington, D.C.

Bergbau-Forschung is presently operating a demonstration plant for the desulfurization of flue gases. The plant accepts 88,275 cfm of flue gas in the form of a slipstream from a 350 MW coal fired boiler owned and operated by STEAG at Kellermann Power Station in Lunen, Federal Republic of Germany. This prototype demonstration unit consists of an adsorption section, a regeneration section and a modified claus unit for reducing SO_2 to elemental sulfur. The demonstration unit at Sneads, Florida consists of an adsorption section, a regeneration section and a RESOX* unit for reducing SO_2 to elemental sulfur.

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*Trademark of Foster Wheeler Energy Corporation.

W.2 DEVELOPMENT OF THE FW-BF PROCESS

The SO_2 removal system developed in the laboratories of Bergbau Forschung in Essen, West Germany is based on and designed for a special activated coke adsorbent.[68] The activated coke, the most critical ingredient in the system, is characterized by excellent SO_2 adsorption, high ignition temperature, and good physical strength and is the result of a research and development program initiated in the late 1950's.

The basic system consists of a gas solid contacting device, the adsorber, and a regenerator which is the desorber. Figure W-1 shows the schematic of the adsorption section. Within the adsorber the activated coke moves downward in the plug flow contained by permanently fixed steel louvers on the gas entrance and exit sides of the unit. The polluted gas stream is passed in through the louvers, through the adsorbent and out of the adsorbent through louvers on the opposite side of the adsorber. The SO_2 contained in the gas stream is initially adsorbed on the inner surface of the activated coke and undergoes subsequent oxidation to sulfuric acid in the presence of the oxygen and water vapor also existent in the polluted gas. Coincidentally, the adsorber also adsorbs NO_x and functions as a panel bed filter for the removal of particulates entrained in the gas stream. The sulfuric acid content of the activated coke increases as a function of coke dwell time in the adsorber; therefore, the coke discharged at the bottom of the adsorber contains the highest possible amount of sulfuric acid for the given conditions and adsorber geometry.

After the adsorbent discharged from the adsorber is separated from particulates by a vibrating sieve, it is regenerated.

The regeneration is effected thermally by heating the sulfuric acid loaded adsorbent in an inert atmosphere. The conditions of regeneration are selected to be sufficient to cause a directional change in the driving forces governing the reactions in this system, whereby the participants undergo a modified

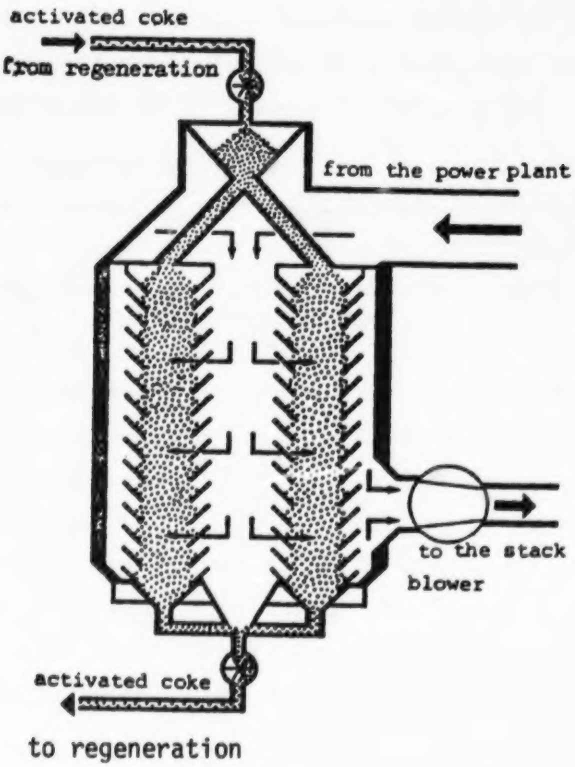
activated coke
from regeneration
from the power plant
to the stack
blower
activated coke
to regeneration

Figure W-1. Adsorption Section - Lunen

reversal of the adsorption reaction, resulting in the reduction of sulfuric acid by the fixed carbon of the adsorbent to yield sulfur dioxide.

The regeneration is carried out in a moving bed reactor utilizing sand as a direct heat carrier to heat the adsorbent to around 650°C (1200°F). The effluent gas of the regeneration contains 20 to 30 percent sulfur dioxide by volume and also H_2O and CO_2. It can then be fed directly to Foster Wheeler's RESOX process for its sulfur dioxide content to be converted to sulfur.

The RESOX process uses coal as a reducing agent to produce elemental sulfur. It was developed in Foster Wheeler Corporation's John Blizard Research Center, and is the result of a research program initiated at the end of the 1960's.

The process is designed to reduce sulfur dioxide contained in an offgas stream to sulfur, and to condense the so produced sulfur product from the gas stream. The RESOX process is capable of handling a wide range of inlet gas compositions, and does not require gas cleaning, drying, or dust removal systems. Crushed coal is the only material and the only catalyst consumed in the process. The process itself represents a new way to achieve the desired degree of reaction between sulfur dioxide and crushed coal at temperatures as low as 650°C (1200°F).

The major process equipment consists of a reactor vessel and a sulfur condenser. In the reactor vessel sulfur dioxide-rich gases are reacted with crushed coal to yield gaseous elemental sulfur. This sulfur is condensed from the gas stream in the sulfur condenser. The high purity liquid sulfur effluent of the process represents a non-polluting by-product.

W.3 PROCESS CHEMISTRY

The process chemistry of the FW-BF Dry Adsorption System for the Adsorption, Regeneration and RESOX sections are described below.

$$SO_2 + C \xrightarrow{Q} CO_2 + S$$

The sulfur is produced in the form of a gas which is subsequently condensed. The nitrogen and carbon dioxide constituents of the Regenerator offgas pass through the RESOX reactor without taking part in the reactions.

The process configuration for the FW-BF Dry Adsorption System at the Scholz Steam Plant is shown schematically in Figure W-2. The system is installed on Boiler No. 2, a nominal 40MW pulverized coal-fired boiler, which has been retrofitted with a sectionalized, high efficiency electrostatic precipitator capable of 99.7% particulate removal.[70]

The system is sized to handle one-half of the total flue gas from this boiler. The 20 MW equivalent in flue gas entering the system is 85,600 ACFM. The flue gas leaving the boiler air pre-heater is at a maximum of 350°F. The system is nominally designed to meet Florida SO_2 reduction codes of 1.2 lb. SO_2/MMBTU heat input which equates to a 74.5% removal efficiency requirement for 3% sulfur, 12,200 BTU/lb fuel. The actual performance of the unit during initial operation far exceeded this requirement.

The equipment utilization and operation of adsorption, Regeneration and RESOX sections is discussed below.

Adsorption is accomplished by passing the flue gas horizontally through vertical columns of activated char in the adsorber. Scholz Steam Plant Demonstration Unit adsorber consists of two vertical stages of char beds designed in a modular fashion. There are eight 6' x 6' beds in the first stage and four 4' x 4' beds in the second stage. All beds are approximately 40 feet high.

The char in the beds is continuously recycled. A conveyor at the top of the adsorber feeds regenerated char into a holding tank which has discharge tubes that gravity feed the regenerated char into the individual char beds. The char moves downward in mass flow adsorbing SO_2 and NO_x as it travels. The char flow

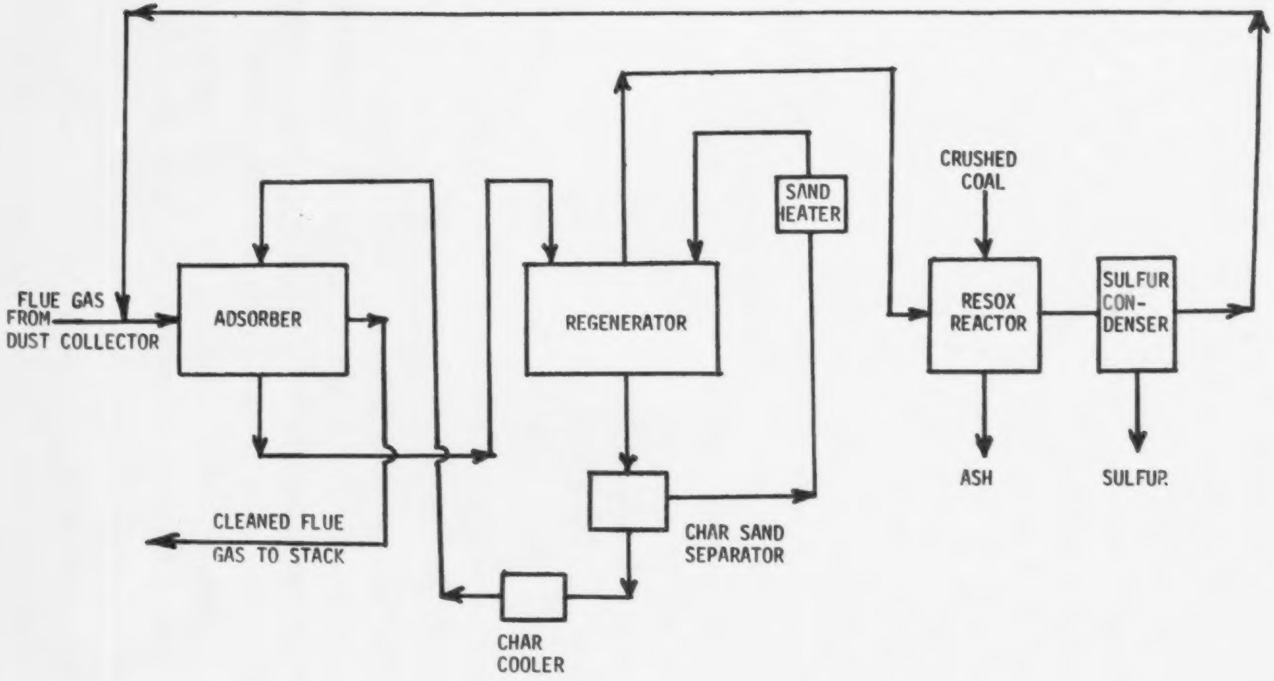
FLUE GAS
FROM
DUST COLLECTOR
ADSORBER
CLEANED FLUE
GAS TO STACK
REGENERATOR
CHAR SAND
SEPARATOR
CHAR
COOLER
SAND
HEATER
CRUSHED
COAL
RESOX
REACTOR
ASH
SULFUR
CON-
DENSER
SULFUR

Figure W-2. FW-BF Dry Adsorption System

rate is controlled by a vibromagnetic feeder at the hopper outlet below each char bed. The saturated char is collected at the discharge of these feeders and sent by a combination of natural frequency conveyors and bucket elevators to the regeneration section of the system.

The flue gas entering the adsorber is tempered, if necessary, by the use of a dilution air fan (vane axial type) which maintains an inlet flue gas temperature of approximately 140°C (284°F). The adsorber discharge fans, one per stage, restore the pressure drop suffered by the flue gas during its passage through the adsorber and associated ductwork.

The regeneration section provides for the continuous onsite regeneration of char which has been loaded with SO_2 in the form of H_2SO_4. Regeneration is achieved by contacting the loaded char with hot sand. Sand is utilized as an inert heat transfer media and as such does not take part in the reactions occurring within the regenerator. Its sole function is to supply heat so that the reactions may take place. The mixture of hot sand and char at 650°C (1200°F) flow slowly downward through the regenerator. Their flow is controlled at the discharge of the regenerator by a char-sand separator-feeder. The char and sand are physically separated by means of a vibrating screen deck. The char is spray cooled to 220°F and returned to the adsorber. The sand is conveyed to a fluidized bed sand heater where heat is added by direct combustion of No. 2 fuel oil. Both the char and sand streams are closed loop operations.

The flue gas produced by the fluidized bed sand heater is used to preheat the incoming combustion and fluidizing air to this heater. After preheating the incoming combustion air, the flue gas goes to the boiler air preheater flue gas inlet for additional heat recovery. It is then injected into the main flue gas stream entering the adsorber, thereby assuring closed loop operation of this gas stream.

The RESOX section provides for the continuous on-site reduction of sulfur dioxide to elemental sulfur. The low volume SO_2 rich offgas stream is directed from the regenerator to the RESOX reactor which is filled with crushed coal. The SO_2 stream is reduced to gaseous elemental sulfur and the liberated oxygen combines with a portion of the coal carbon to form carbon dioxide. The gases leaving the reactor enter a sulfur condenser where the sulfur is condensed to molten elemental sulfur. The sulfur is collected and stored in an insulated tank (which is equipped with steam heating coils to make up for heat losses through the insulation system) to maintain the sulfur in a molten form pending shipment via tank truck. The mass-flow coal movement through the reactor is controlled by a discharge feeder. The combination of non-consumed coal and ash is fed into a receiver vessel for ultimate disposal after cooling. The tail gases leaving the sulfur condenser consist of CO_2, H_2O, N_2 and those remaining "S" values not converted to elemental sulfur. The gases are recycled to the boiler via a centrifugal blower where the sulfur values are oxidized to SO_2 and then re-enter the adsorber allowing complete closed loop operation of the unit.

W.4 PW-BF SCHOLZ STATION DRY ADSORPTION SYSTEM PERFORMANCE

During the start up of the Lunen demonstration unit, some mechanical problems were encountered in the adsorption and the regeneration sections. But according to Mr. W.F. Bischoff of Foster Wheeler Energy Corporation,[71] the adsorption and regeneration sections are reasonably well optimized now. He adds that the only major problem existing at Lunen is the proper functioning of the modified Claus unit. Foster Wheeler is currently looking for funding to install a RESOX unit to replace the Claus unit at Lunen and then test the integrated system.

Foster Wheeler[72] reports the power consumption for the whole system to be between 0.6 and 1.5 percent of steam generator name plate rating depending on the system design and the mode of operation. Another point of interest is the SO_2 removal efficiency. Removal efficiency is a function of several parameters including SO_2 concentration at inlet, inlet flue gas temperature, char dwell time and gas residence time. In the brief period of operation with diverse operating conditions, SO_2 removal efficiencies were between 96 and 100 percent consistently. Another point noted during the operation was that the exit gases from the adsorber were 0 to 30°F higher than inlet to the adsorber, thereby increasing the buoyancy of the stack gases.

Based on present information the FW-BF Dry Adsorption System appears technically feasible but requires full-scale operating time and data to prove itself.

APPENDIX X

SULFUR/SULFURIC ACID PRESENT AND FUTURE USES AND MARKETS

X.1 SOURCES

Over the past centuries, there have been many fundamental changes in sulfur/sulfuric acid supply sources. Early civilizations obtained their meager requirements from native sulfur deposits in or near volcanoes. The increase in demands in the late 1700's and early 1800's was largely satisfied by the development of native sulfur deposits in Sicily. Monopolistic practices by the Sicilians, which resulted in exorbitant price levels, caused consumers to shift to pyrites as their major source of supply during the second half of the 1800's.

For many years pyrite, iron disulfide, was the main sulfur-containing material in the manufacture of sulfuric acid. In 1895, Herman Frasch developed his process for extracting sulfur from underground deposits by injecting hot water into the deposit, melting the sulfur, and recovering it in liquid form. The exceptional purity and quality of sulfur appealed to the chemical industry, particularly to the manufacturers of sulfuric acid. As a consequency, Frasch's sulfur supplanted practically all other raw materials formerly used in the manufacture of sulfuric acid. The development of the Frasch process for mining the large native sulfur deposits associated with the salt domes in Texas and Louisiana created a new and important source of high purity elemental sulfur for domestic and world markets. As a result, the United States became the world leader in sulfur production in 1913, and it has never relinquished this lead.

Frasch sulfur and pyrites have continued to maintain their joint predominant positions as world sources of sulfur to the present time, but they are being rapidly challenged by new sources of sulfur produced as co-products or byproducts. The trend started about 1950 with rapid increases in the production of elemental sulfur at refineries and natural gas treatment plants and of byproduct sulfuric acid at nonferrous smelters. The pyrites sector of the sulfur industry is being seriously affected by the latter developments.

X.2 PRESENT USES

Sulfur is unusual as compared with most major mineral commodities in that by far the largest portion of it is used as an intermediate in the manufacture of other chemical products. Sulfuric acid is the most important of these intermediate products. Ninety precent of the sulfur consumed in the United States in 1975 was either converted to sulfuric acid or produced directly in this form. Other intermediate products were carbon disulfide and sulfur dioxide, each of which accounted for 3% of the total sulfur consumption. Only 4% of the total consumption was used directly in the elemental form. The use of sulfur in U.S. by end-use categories is as follows:

- Agriculture (Fertilizers) - This category is by far the most important, accounting for 55% of domestic sulfur demand. The principal individual requirement is for the manufacture of phosphatic fertilizers, with sulfuric acid being the essential intermediate sulfur product being used. Another individual, but relatively small, end-use within this category is the production of ammonium sulfate by the reaction of sulfuric acid with ammonia. Additionally, a small amount of sulfur in elemental form or in the form of gypsum is used as a soil conditioner and plant nutrient. This latter use of sulfur is growing in importance because the higher grade phosphatic fertilizers now being produced by the wet phosphoric acid process do not have the needed sulfur content that was a component of the older, lower grade fertilizer products.

- Plastic and Synthetic Products - This category covers a wide range of synthetics including acetate, cellophane, rayon, and various products, fibers and testiles. The sulfur intermediates involved in their manufacture were equally divided between sulfuric acid and carbon disulfide.

- Paper Products - In this category, the largest single segment of demand is in the manufacture of wood pulp by the sulfate process. In this process, the major sulfur intermediate is sulfur dioxide, generally produced at the plant site by burning elemental sulfur, although some sulfur dioxide is produced as a byproduct at smelter operations, purified and liquified, and shipped to the pulp mills.

- Paints - The major sulfur use in this category is for the production of titanium dioxide pigment by the sulfate process. Difficulties in the disposal of ferrous sulfate waste product has led to the development of the hydrochloric acid process.

- Nonferrous Metal Production - This category covers the leaching of copper and uranium ores with sulfuric acid. In the case of copper, it is used for the extraction of metal occurring in deposits, mine dumps, and wastes whose copper contents are too low to justify concentrations by conventional floatation techniques, or for recovery of copper from ores containing copper carbonate and silicate minerals, which generally cannot readily be treated by floatation processes. The sulfuric acid required for copper leaching is invariably the byproduct sulfuric acid produced by the copper smelters in the area.

  Sulfuric acid is the most commonly used reagent for the recovery of uranium from ores. The sulfuric acid used is either the byproduct sulfuric acid produced at smelters or sulfuric acid produced from elemental sulfur.

- Explosives - In this category sulfur is used entirely in the form of sulfuric acid. Sulfuric acid is not only used in direct manufacture of explosives, but numerous related nitration processes.

- Petroleum Refining - This category includes not only petroleum refining as such, but associated chemical processes where process streams may serve both the refinery and the chemical complex. The major idetnified end use for sulfuric acid is as a catalyst for alkylation, a process by which liquid high-octane gasoline components with very good stability may be produced by a combination of gaseous streams. Sulfuric acid and hydrofluoric acid are competing catalysts in this process. Sulfuric acid for refinery processes is manufactured from recovered sulfur produced at the refinery and from contaminated acid (acid sludge) returned to the acid plants for reconstitution.

- Iron and Steel Production - Sulfuric acid is used as a pickling agent to remove mill scale, rust, dirt, and grease from the surface of steel products prior to further processing. The sulfuric acid pickling process faces increasing competition from hydrochloric acid, largely because of the problem of disposing of the ferrous sulfate waste product. Although there are both advantages and disadvantages in the use of hydrochloric acid, it appears that it will largely replace sulfuric acid over the long range. There is no well-defined source of sulfuric acid for steel pickling since it is generally obtained from merchant sulfuric acid plants that use the cheapest form of sulfur available in the area in which it is produced.

- Other Uses - This general category covers a wide variety of end uses, including intermediate chemical products. These miscellaneous uses, especially those involving sulfuric acid, are intimately associated with practically all elements of the nation's industrial and chemical complexes.

X.3 NEW USES FOR SULFUR[73,74]

For some time now, organizations in the sulfur industry have been involved in the development of new uses for sulfur. The research is directed towards the developments of new uses that would

(a) consume large volumes of sulfur, (b) are economically favorable to attract industry interest and capital, (3) are non-polluting, and (d) are not costly to produce.[75]

One of the major developments for new uses in recent years has been that of a sulur-asphalt paving material called "Thermopave" by Shell Canada.[76,77] The product contains 13% sulfur, 6% asphalt and 81% sand, and possess considerable commercial acceptance. It is economically attractive, has superior properties when compared to the conventional asphalt-aggregate paving materials and would use large amounts of sulfur.

A foam which is lighter than water with compressive strength comparatively higher than that of typical organic polymers has also been developed.[78] Its potential uses are, for instance, thermal insulation and general building insulation.

The manufacture of sulfur concrete involves the mixing of molten sulfur (350°F) with sand or aggregate, in the ratio 30:70, and then letting the mixture cool and harden, either to form bricks, blocks, tiles or other structural materials. Other potential uses of this product are concrete pipes, slip-forming of street curbs, traffic barriers, etc.[79] Indeed there is a huge potential for exploiting and establishing markets for such a product, but as yet it is still in the early stages of development.

Research in various other uses of sulfur has been carried out.[80] Included in these are: (a) the use of sulfur as a coating material providing resistance against corrosion and errosion, and (b) as a surface bonding material, providing a hard and impervious surface on a wall that would not require mortar or joining material between blocks.

However, while some of these products have already been developed and tested successfully, it is highly unlikely that any of them will be commercially produced on a significant scale prior to the end of this decade. It should be noted that the research in the development of new products such as discussed above was stimulated by the prospects of a sulfur surplus.

The use of sulfuric acid injected directly into the soils in Arizona looks very promising.[81] This procedure tends to break up the adobe soil as well as decrease the pH to a more favorable range for agriculture. Yields have definitely increased and it is considered one of the promising future potential markets. Approximately 4,000-5,000 tons per month of acid are presently being used for this purpose.

X.4 PRESENT PRODUCTION AND CONSUMPTION

Sulfur in its different forms is produced worldwide with no one country being a producer or supplier to world markets. In 1974, world production of sulfur in terms of sulfur content of the product produced amount to 50.9 million tons.[82] The United States was the leading producer, accounting for 22% of the output. A tablulation of world sulfur production in 1973 and capacities for 1973, 1974 and 1980 is shown in Table X-1. The total U.S. production of sulfur in 1975 was 11.26 million tons. The salient sulfur statistics for the years 1971 to 1975 is given in Table X-2.

Sulfur for domestic consumption was obtained mainly from domestic sources: Frasch 45%, recovered elemental 27%, and sulfur in other forms 10%. The remaining 18% of the sulfur was obtained by imports of Frasch and recovered elemental sulfur. In 1975, Frasch sulfur accounted for 64% of the domestic production.[83] Frasch sulfur was produced at 13 mines in Texas and Louisiana. Duval Corporation, with one mine in Texas, Freeport Minerals Company, with four mines in Louisiana, and Texas Gulf, Inc., with five mines in Texas and one mine in Louisiana, accounted for most of the Frasch production. The five largest mines, with a production rate in excess of one-half million tons per year each, accounted for 84% of the total Frasch sulfur output. They also accounted for 54% of the total production of sulfur in all forms during 1975.

Recovered elemental sulfur accounted for 26% of the total domestic production of sulfur in all forms[84]. It was produced by fifty-six companies at 140 plants in 28 states, one plant in the Virgin Islands, and one in Puerto Rico. Most of the plants were relatively small size, with only five of them reporting an annual production exceeding 100,000 tons. By source, 55% was produced by 38 companies at 79 refineries or satellite plants treating refinery gases, and two coking operations, and 45% was produced by 29 companies at 59 natural gas treatment plants.

Table X-1. WORLD SULFUR PRODUCTION 1973 AND CAPACITY 1973, 1974, AND 1980

(Thousand long tons)

	Production	Capacity		
	1973	1973	1974	1980
North America:				
United States	10,921	12,000	13,000	15,000
Canada	7,779	8,000	8,000	7,000
Mexico	1,650	1,900	2,500	3,000
Other	100	200	200	200
Total	20,450	22,100	23,700	25,200
South America	300	400	600	1,100
Europe:				
U.S.S.R	7,500	8,000	8,500	12,000
Poland	3,600	4,000	4,000	4,000
France	2,000	2,500	2,500	2,500
West Germany	1,050	1,200	1,400	1,600
Spain	1,000	1,200	1,400	1,400
Italy	800	900	900	900
Other	2,700	3,000	3,300	3,800
Total	18,650	20,800	22,000	26,200
Africa	600	700	700	800
Asia:				
Japan	3,000	3,500	4,000	5,000
Near East	1,250	1,500	2,000	5,000
China	1,200	1,300	1,300	1,800
Other	250	300	300	400
Total	5,700	6,600	7,600	12,200
Oceania	300	400	400	500
World Total	46,000	51,000	55,000	66,000

Source: Ref. 85

Table X-2. SALIENT SULFUR STATISTICS
(Thousand long tons, sulfur content)

	1971	1972	1973	1974	1975
Production:					
Frasch	7,025	7,290	7,605	7,901	7,211
Recovered elemental	1,595	1,950	2,416	2,632	2,969
Byproduct sulfuric acid	518	546	600	654	767
Pyrites	316	283	212	162	237
Other forms 1/	126	149	88	70	75
Total	9,580	10,218	10,921	11,419	11,259
Shipments (Sold or used):					
Frasch	6,738	7,613	7,438	7,898	6,077
Recovered elemental	1,582	1,927	2,451	2,547	2,902
Byproduct sulfuric acid	518	546	600	654	767
Pyrites	316	283	212	162	237
Other forms 1/	126	149	88	70	75
Total	9,280	10,518	10,789	11,331	10,058
Imports:					
Frasch (Mexico)	449	269	302	954	967
Recovered elemental (Canada)	850	868	905	1,194	930
Recovered elemental (Other)	---	1	15	2	2/
Pyrites (Canada)	130	50	---	---	---
Total	1,429	1,188	1,222	2,150	1,897
Exports:					
Crude 3/	1,532	1,847	1,771	2,580	1,288
Refined 3/	4	5	5	21	7
Crude, recovered elemental, from the Virgin Islands	---	---	---	62	57
Total	1,536	1,852	1,776	r/2,663	1,352
Apparent Consumption 4/:					
Frasch - Domestic	5,202	5,761	5,662	5,297	4,782
Imports	449	269	302	954	967
Recovered elemental					
Domestic	1,582	1,927	2,451	r/2,485	2,845
Imports	850	869	920	1,196	930
Byproduct sulfuric acid	518	546	600	654	767
Pyrites - Domestic	316	283	212	162	237
Imports	130	50	---	---	---
Other forms 1/	126	149	88	70	75
Total	9,173	9,854	10,235	r/10,818	10,603
Yearend Producers' Stocks 5/:					
Frasch	4,023	3,665	3,816	3,744	4,857
Recovered elemental	97	131	111	213	269
Total	4,120	3,796	3,927	3,957	5,126

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r/ Revised.
1/ Hydrogen sulfide and liquid sulfur dioxide.
2/ Less than 1/2 unit.
3/ Accounted for as Frasch sulfur.
4/ Measured as shipments, plus imports, minus exports.
5/ Reported producers' stocks after inventory adjustments.

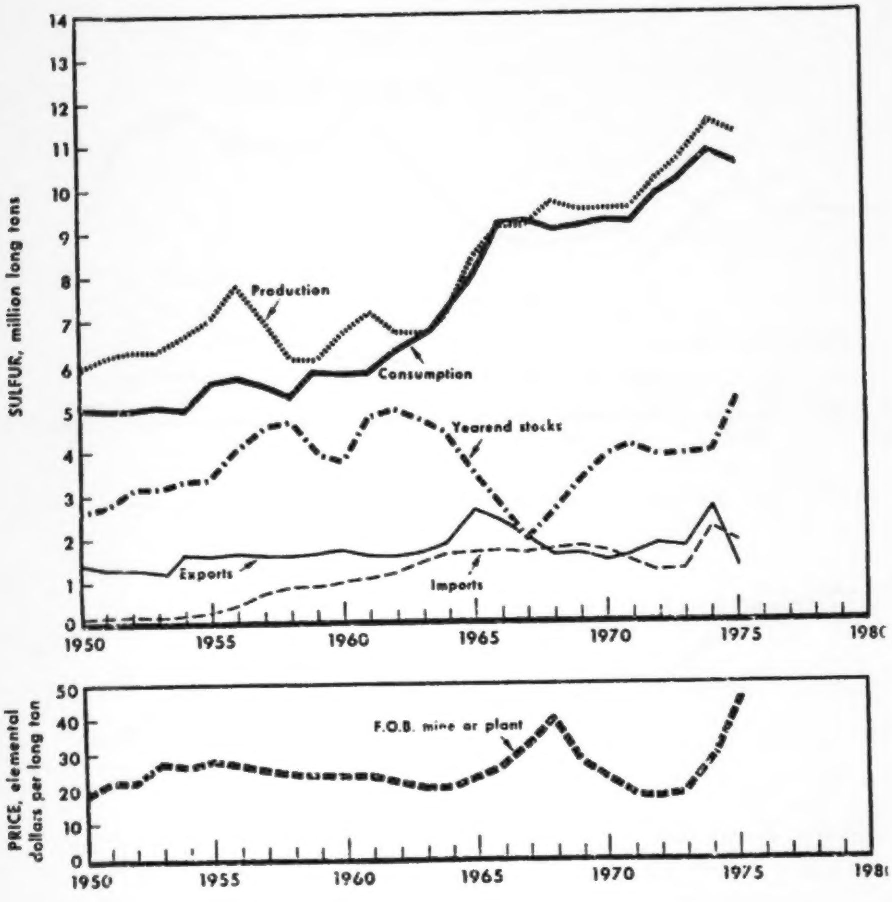
Source: Reference 86

Sulfur contained in by product sulfuric acid produced at copper, lead and zinc roasters and smelters during 1975 amounted to 7% of the total domestic production of sulfur in all forms.[87] It was produced by 12 companies at 22 plants in 13 states. Twelve acid plants operated in conjunction with copper smelters, and 10 plants operated as accessories to lead and zonc roasting and smelting operations. The five largest producers of byproduct sulfuric acid were American Smelting and Refining Company, Magma Copper Company, Kennecott Copper Corporation, Phelps Dodge Corporation, and St. Joe Minerals Corporation. Together, their 13 plants produced 68% of the output during 1975.

Contained sulfur in pyrites, hydrogen sulfide, and sulfur dioxide amounted to 3% of the total production in all forms during 1975.[88] Pyrites were produced by three companies at three mines in three states; hydrogen sulfide by four companies of five plants in four states; and sulfur dioxide by two companies at two plants in two states. The three largest producers of these products were Cities Service Company (pyrites, hydrogen sulfide and sulfur dioxide), American Smelting and Refining Company (sulfur dioxide), and Shell Oil Company (hydrogen sulfide). Together, their one mine and five plants accounted for 93% of the contained sulfur produced in the form of these products.

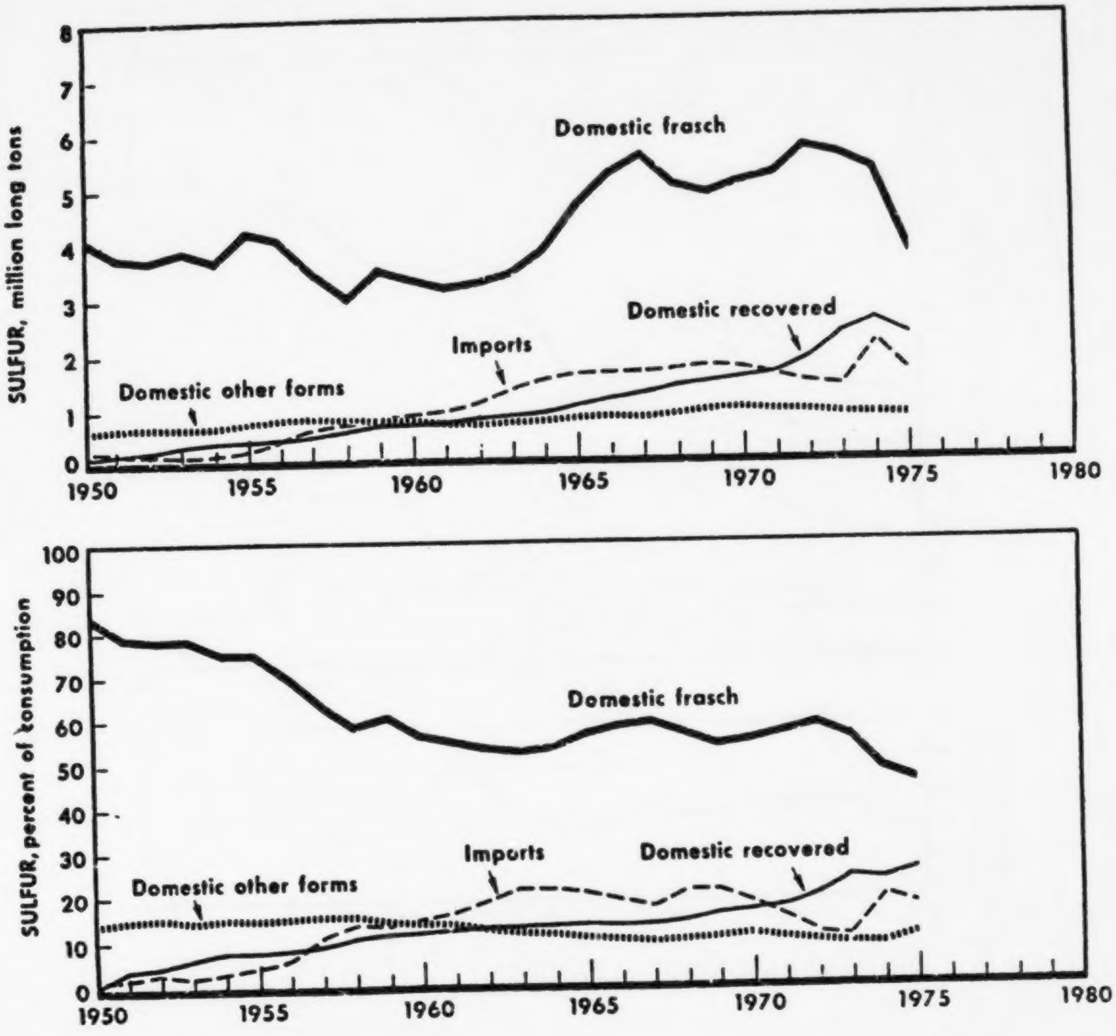
The trends in the sulfur industry in the United States for the past twenty-five years is given in Figures X-1, X-2, and X-3. The sulfur produced and shipped from Frasch mines in the United States, by-product sulfuric acid produced in the United States, and pyrites, hydrogen sulfide and sulfur dioxide sold or used in United States is given in Tables X-3, X-4, X-5, and X-6 respectively. The trends in the sulfur production and consumption in the United States for the past twenty-five years is given in Figures X-2 and X-3 respectively. The sulfur supply-demand relationships and end-use for the years 1964 and 1974 is given in Table X-7.

Arthur D. Little[92] gives the U.S. sulfuric acid capacity for 1975 in Table X-8. As indicated in Table X-8, U.S. sulfuric



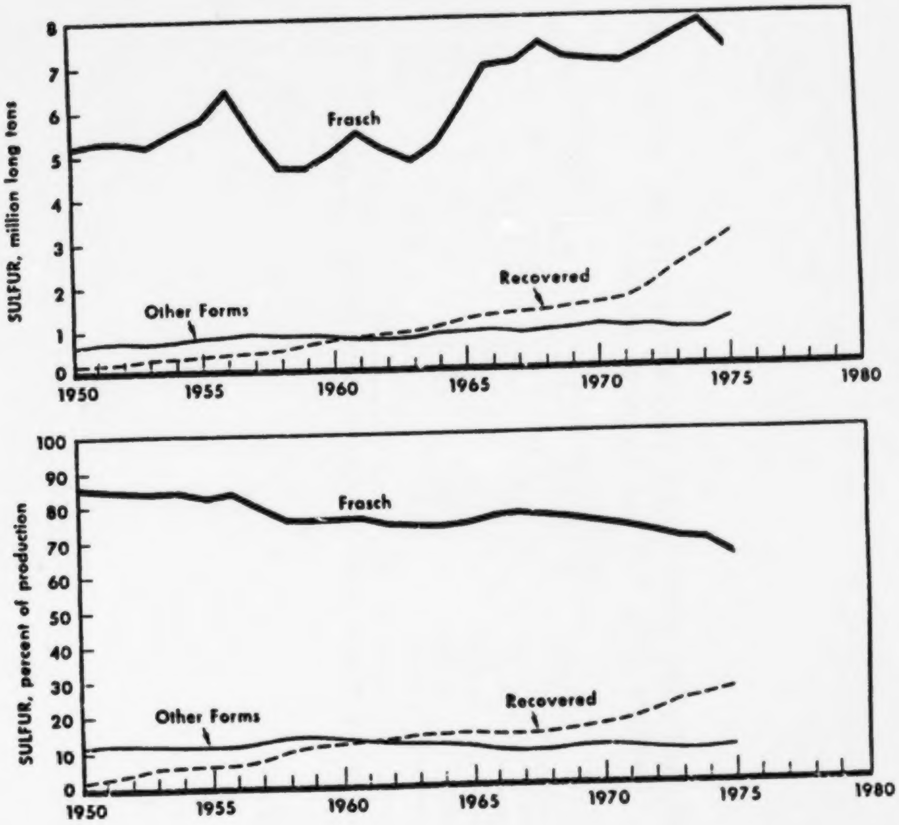
Source: Reference 89

Figure X-1. TRENDS IN THE SULFUR INDUSTRY IN THE UNITED STATES



Source: Reference 90

Figure X-2. TRENDS IN THE CONSUMPTION OF SULFUR IN THE UNITED STATES



Source: Reference 91

Figure X-3. TRENDS IN THE PRODUCTION OF SULFUR IN THE UNITED STATES

Table X-3. SULFUR PRODUCED AND SHIPPED FROM FRASCH MINES IN THE UNITED STATES
(Thousand long tons and thousand dollars)

Year	Production			Shipments	
	Texas	Louisiana	Total 1/	Quantity	Value 2/
1971	3,408	3,616	7,025	6,738	117,894
1972	3,755	3,534	7,290	7,613	132,385
1973	4,294	3,311	7,605	7,438	138,578
1974	4,593	3,308	7,901	7,898	241,066
1975	4,141	3,070	7,211	6,077	304,843

1/ Data may not add to totals shown because of independent rounding.
2/ F.o.b. mine.

Source: Reference 97

Table X-4. RECOVERED SULFUR PRODUCED AND SHIPPED IN THE UNITED STATES
(Thousand long tons and thousand dollars)

Year	Production			Shipments	
	Natural gas plants	Petroleum refineries	Total 1/	Quantity	Value 2/
1971	638	957	1,595	1,582	27,483
1972	819	1,131	1,950	1,927	30,050
1973	1,046	1,370	2,416	2,451	37,873
1974	1,219	1,414	2,632	2,547	60,599
1975	1,342	3/1,627	2,969	2,902	104,886

1/ Data may not add to totals shown due to independent rounding.
2/ F.o.b. plant.
3/ Includes a small quantity from coking operations.

Source: Reference 98

Table X-5. BY-PRODUCT SULFURIC ACID (SULFUR CONTENT) PRODUCED IN THE UNITED STATES
(Thousand long tons and thousand dollars)

Year	Copper plants 2/	Lead and zinc plants 3/	Total	Value
1971----------------------	234	284	518	21,293
1972----------------------	295	251	546	22,897
1973----------------------	318	282	600	24,175
1974----------------------	373	281	654	29,370
1975----------------------	521	246	767	42,956

1/ Includes acid from foreign materials.
2/ Excludes acid made from pyrites concentrates.
3/ Excludes acid made from native sulfur.

Source: Reference 99

Table X-6. PYRITES, HYDROGEN SULFIDE AND SULFUR DIOXIDE SOLD OR USED IN THE UNITED STATES
(Sulfur Content)
(Thousand long tons and thousand dollars)

Year	Pyrites	Hydrogen Sulfide and Sulfur Dioxide	Total	Value
1971	316	126	442	9,530
1972	283	149	432	9,227
1973	212	88	300	7,188
1974	162	70	232	6,052
1975	237	75	312	7,097

Source: Reference 100

Table X-7. SULFUR SUPPLY-DEMAND RELATIONSHIPS, 1964-74
(Thousand long tons)

	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974
World production:											
United States	7,087	8,196	9,141	9,121	9,735	9,545	9,557	9,580	10,218	10,921	11,419
Rest of world	20,813	21,804	22,559	24,579	25,565	27,655	29,643	31,320	32,782	35,079	39,481
Total	27,900	30,000	31,700	33,700	35,300	37,200	39,200	40,900	43,000	46,000	50,900
Components of U.S. supply:											
Domestic mines	7,087	8,196	9,141	9,121	9,735	9,545	9,557	9,580	10,218	10,921	11,419
Imports	1,582	1,646	1,674	1,639	1,754	1,795	1,667	1,429	1,188	1,222	2,150
Industry stocks, Jan. 1	4,683	4,403	3,425	2,704	1,954	2,655	3,338	3,829	4,120	3,796	3,928
Total	13,352	14,245	14,240	13,464	13,443	13,995	14,562	14,838	15,526	15,939	17,497
Distribution of U.S. supply:											
Industry stocks, Dec. 31	4,403	3,425	2,704	1,954	2,655	3,338	3,829	4,120	3,796	3,928	3,957
Exports	1,928	2,635	2,373	2,193	1,602	1,551	1,433	1,535	1,852	1,777	2,601
Demand	7,255	7,981	9,145	9,251	9,072	9,169	9,227	9,173	9,854	10,234	10,880
Apparent surplus (+), deficit (−) of supply[1]	−234	+204	+18	+66	+114	−63	+73	+9	+24	----	+59
U.S. demand pattern:											
Agriculture (fertilizers)	3,090	3,810	4,425	4,735	4,470	4,465	4,680	4,800	5,210	5,520	5,930
Plastic and synthetic products	500	555	555	495	550	570	495	515	540	580	610
Paper products	415	430	440	400	390	365	350	320	340	370	390
Paints	505	510	520	505	490	445	420	300	390	420	440
Nonferrous metal production (Cu-U)	235	265	310	260	300	370	390	410	430	500	560
Explosives	215	230	260	265	250	260	255	255	260	280	290
Petroleum refining	155	165	190	195	180	190	195	200	220	230	240
Iron and steel production	330	295	275	220	170	125	120	105	110	110	110
Other	1,810	1,921	2,170	2,176	2,272	2,379	2,322	2,188	2,354	2,224	2,260
U.S. primary demand	7,255	7,981	9,145	9,251	9,072	9,169	9,227	9,173	9,854	10,234	10,880

[1] The difference between total U.S. distribution of supply and total U.S. supply.

Source: Reference 101

Table X-8. U.S. SULFURIC ACID CAPACITY - 1975

Producer		Annual Capacity (Thousand tons)
A. Northwest		2,158
B. California		1,702
C. Southwest		3,787
	(Western U.S. Subtotal	7,647)
D. Other U.S.		38,748
		46,395

Source: Reference 102

acid capacity in 1975 was approximately 46 million tons. The vast majority of this capacity (84%) is in the Gulf Coast and eastern U.S. The Northwest, the Pacific Coast, and the Southwest, together accounted for only 16 percent of the U.S. sulfuric acid capacity.

United States Department of Commerce in their Current Industrial Reports[93] report sulfuric acid production in U.S. by area for the years 1973 and 1974. This production distribution is given in Table X-9.

There are a wide range of government programs that are designed not only to increase the production of sulfur but to protect the environment from the effects of sulfur dioxide emissions and to develop new uses for sulfur. The Bureau of Land management[94] has a leasing program for native sulfur on public lands in Louisiana, New Mexico, and the outer continental shelf. The Office of Minerals Exploration lends up to 50% of approval costs for sulfur exploration. The Bureau of Mines[95] is conducting research on the recovery of sulfur from smelter gases and industrial stack gases. The Department of Energy is doing extensive research and development on gasification and liquefaction of coal. The sulfur recovery potential from these processes would be very great if commercialized. The Environmental Protection Agency has a wide range of research programs primarily aimed at reducing sulfur dioxide emissions. The Bureau of Mines[96] has a research program aimed at developing new uses for sulfur of a magnitude that would alleviate a potential over supply problem.

X.5 FUTURE MARKET PROJECTIONS

World sulfur or "brimstone" trading is expected to maintain a steady growth between 1977-80 to reach 21.2 million tons. The higher rate of growth up to 1980 is largely attributable to the anticipated recurrence in the strength of demand from the fertilizer industry. Almost 57% of the projected 12.7 million tons increase in brimstone output between 1976 and 1985 is forecast to be in the form of recovered (not mined) sulfur.[104] In fact, for the first time recovered sulfur output will exceed that of Frasch and native refined sulfur.

Table X-9. SULFURIC ACID: PRODUCTION OF NEW ACID, BY AREA: 1974 AND 1973

(In 1,000 short tons of 100% H_2SO_4)

Reproduced from best available copy.

Area	1974[1]	[r]1973[1]
UNITED STATES, TOTAL	32,233.6	30,391.5
New England[2]	168.3	150.8
Middle Atlantic	2,346.4	2,433.4
Pennsylvania	689.4	777.9
New York and New Jersey	1,657.0	1,655.4
North Central	3,449.5	3,773.9
Illinois	966.5	1,084.0
Indiana	522.9	643.9
Michigan	96.9	100.9
Missouri	482.0	546.4
Ohio	578.5	560.4
Other[3]	792.7	838.3
South	22,667.0	20,624.3
Alabama	356.8	376.0
Arkansas	342.8	354.6
Florida	9,092.8	8,554.0
Georgia	527.6	504.1
Louisiana	4,326.0	3,746.3
North Carolina	1,498.7	1,072.4
Virginia	713.9	705.7
Texas and Oklahoma	3,309.9	2,764.3
Delaware and Maryland	670.8	703.4
Other[4]	1,837.7	1,843.3
West	3,602.3	3,409.3
Arizona	492.6	384.0
California	1,416.0	1,385.3
Washington	130.4	138.8
Other[5]	1,563.3	1,514.3

Note: Detailed figures may not add to totals because of independent rounding in computer operations.

[r] Revised.
[1] Includes data for Government-owned, privately operated plants.
[2] Includes data for plants located in Maine, Massachusetts, and Rhode Island.
[3] Includes data for plants located in Wisconsin, Minnesota, Iowa, and Kansas.
[4] Includes data for plants located in West Virginia, Kentucky, Tennessee, Mississippi, and South Carolina.
[5] Includes data for plants located in Colorado, Montana, Wyoming, New Mexico, Utah, Nevada, Hawaii, and Idaho.

Source: Reference 103

Canadian and French recovered sulfur output is projected to decline by 2.2 million tons but this fall will be more than compensated by an increase of some 3.9 million tons in the Arabian Gulf recovered sulfur output.[105] Frasch and/or native sulfur mining in Mexico, Poland, Iraq and the USSR will maintain a steady growth. The brimstone supply/demand situation in the 1980's may give rise to large scale exploitation of sulfur deposits in other areas, such as Bolivia.

In the September 27, 1976 issue of Chemical Engineering,[106] the conflicting views of experts on the sulfur supply and demand situation in the coming years is presented. Marked change in the balance of supply of brimstone from mining, hydrocarbon sweetening and pollution control, as well as restructuring of the market for the material, complicates sulfur's outlook over the next decade.

Controversy over sulfur is not a new phenomenon. While the material finds customers in a broad range of sectors within the chemical process industries and elsewhere, its demand has remained cyclical, tied to the fortunes of the key-market-phosphatic fertilizers. Now, the picture is clouded by a number of new factors.

On the surplus side: existing world stockpiles of a record 26 million tons of surplus sulfur; the likelihood of large tonnages of recovered sulfur being produced in the Middle East as a result of sweetening operations at natural-gas-exploitation project underway there; the probability of more sulfur being recovered as a result of U.S. and Western European environmental legislation targeted at power-plant stack-gas emissions; the virtual certainty that more high-sulfur crude will be processed in the U.S.; and the expected growth of recovered sulfur supplies following commercialization of projects for synthetic natural gas, coal liquefaction, shale oil and other alternative energy sources.[107]

On the shortage side: predicted declines in sulfur associated with dwindling gas-fields in currently strong producing areas such as France and Canada; doubts about the rate of growth of recovered sulfur in the next decade; lack of strong economic incentives for continued growth of Frasch (mined) sulfur production in U.S.; reservations about the marketability of small tonnages of recovered sulfur from scattered individual sources; and rapidly inflating capital costs for Frasch facilities, recovery units and shipping and transportation.[108]

On the consumption side, some of the sectors in industry will cut their sulfuric acid requirements and consequent demand for suflur. In the wood pulp industry, there is a swing to making less use of the sulfate process. In the paint industry, there is a swing to making titanium dioxide pigment by the chloride route, phasing out the sulfate route (with its byproduct problems). And in steel pickling, hydrochloric acid is rapidly replacing sulfuric acid.

One expanding industry that will call for more sulfuric acid is non-ferrous-metal production (especially copper and uranium), where annual growth of sulfur demand will probably hold at 4.2%.[109] Most of the sulfuric acid in the copper industry will come from recovery plants at the smelter.

Recovered-sulfur output figures are a strong factor supporting theorists who predict a surplus. In the U.S., according to one industry source, elemental sulfur from petroleum and natural gas operations may mount to 4.6 million tons annually by the end of the decade and continue to grow in subsequent years, perhaps reaching 4.9 million tons/hr by 1985, in another, more conservative estimate.[110]

But at last October's London meeting of the European Chemical Market Research Association, Martin Horseman, a director of the British Sulfur Corporation (London) reported that the world growth in recovered sulfur would be far less spectacular during the next ten years than it was during the 1965-74 period.[111] He added that between 1975-85, sulfur production from hydrocarbon process is anticipated to increase at a rate of some 3.6% per annum, compared with a rate of 11.7% per annum between 1965-74.

Texas Gulf's Rittenhouse,[112] speaking at a May meeting of the U.S.'s Chemical Market Research Association (CMRA) predicted that byproduct sulfur production in U.S. may total only 8 million tons/yr as compared to earlier preductions of 20 million tons.

U.S. Bureau of Mines[113] on the other hand, is still confident that recovered sulfur will continue to carve itself a large share of the worldwide market. Subject to suitable technology emerging, and continued environmental constrains, the Bureau predicts that co-product sulfur output in the U.S. will rise from 31% of total production to 83% by the year 2000, accounting for 87% of U.S. supplies.

The big question mark hanging over recovered-sulfur output is that of environmental legislation. The basic imponderables here are: When will coal gasification start to make inroads as an energy source, and how much sulfur will be recovered in a usable form from stack gases, rather than lost because of the use of cleanup technology that discards sulfur values?

Exxon[114] estimates that, by 1985, coal gasification will contribute a maximum 200,000 tons/yr of sulfur, and shale oil will yield only 100,000 tons/yr because sulfur in shale oil is mainly retained in the shale as sulfate. Texas Gulf and the Sulfur Institute are equally pessimistic, seeing these sources developing slowly, too. Texas Gulf's Rittenhouse[115] wonders whether environmental legislation will have much effect on sulfur recovery at power plants, since at the present there are hardly any commercial power plants that are recovering sulfur.

Figures from the National Coal Association (Washington, D.C.)[116] based on Project Independence projections, show that 1985 total coal consumption will reach 1,140 millon tons against 1975's 620.2 million tons. Electric utilities will be burning at least

715 million tons/yr of coal in 1985, and more probably as much as 826 million tons, says NCA. But how much sulfur will be contained in the coal, or how much of this material will actually be recovered, no one is inclined to speculate about.

Canadian sulfur production, from Western Canadian sour-gas plants, will decline as a major source, all authorities agree.[117] Output of Canadian sulfur peaked in 1973-74 at just over 7 million tons/yr, and fell in 1975 to 6.5 million tons. Production will drop to 5.7 million tons/yr in 1980 and 3.7 million tons/yr in 1985, Texas Gulf estimates. The chances of new discoveries halting this slide are slim too.

The impact of increased Middle East recovered-sulfur output is difficult to estimate. Projects to harness previously-flared natural gas will start up in the 1980's, turning out large tonnages of sulfur too. In Saudi Arabia, for example, Aramco plans sulfur-recovery facilities turning out 7,000 tons/d. Rittenhouse[118] pegs current production in the area at 1.4 million tons/hr, mostly in Iraq, which has a domestic Frasch industry, and Iran. He estimates that production should double by 1980 and that by 1985, output could be as much as 4.0 million, but will certainly reach 3.0 million tons.

The U.S. Frasch industry has viewed the growth of recovered sulfur with concern intensified by soaring Frasch process energy costs, and increasing capital costs for new mining and transportation facilities. Increasing costs or exhaustion of reserves have closed ten mines in the 1970's, including five within the last year.[119]

Predictions for future Frasch output vary, but none are optimistic. According to Exxon,[120] U.S. Frasch production may fall to 6.6 million tons/yr or less by 1985. Another source predicts an even sharper falloff: output at 7.4 million tons/yr in 1980, dropping to a tentative 5.7 million tons by 1985. The views of Westinform Service Ltd.[121] on sulfur also tend to support reduction or minimum expansion of Frasch.

Forecasts of U.S. and rest-of-world sulfur demand for 1985 and 2000 is given in Table X-10. The U.S. sulfur demand in 2000 is forecast to range between 18 and 26 million tons.[122] The probable range within this range is set at 14.5 million tons in 1985 and 23 million tons in 2000. This represents a probable average annual growth rate of 3%. The growth rate of the probable demand in the rest of the world is expected to be somewhat greater, about 3.7%. This faster rate is due to relatively more rapid industrial expansion in the developing countries of the world. In summation, the most probably world demand in 2000 is estimated to be 110 million tons at a growth rate of 3.5%.[123]

The demand forecasts for domestic end uses are shown in Table X-11. They were developed by U.S. Department of Interior[124] by applying the growth rate of selected economic indicators to the patterns of end uses and projecting to 2000 to establish a forecast base for each use. The economic indicators used for establishing the forecast bases were as follows: phosphate rock consumption in fertilizers as an agricultural indicator; population as a paper products indicator; and the Federal Reserve Board Index of Industrial Production as an indicator for all other end uses. In the case of paints, and iron and steel production, neither a forecast base or forecast range was established because it is anticipated that these uses will be phased out by 2000.

The sulfur supply pattern is expected to be drastically restructured by 2000. Production from primary (Frasch) sources will be gradually phased out and replaced by production from environmental-related co-product sources.[125] Table X-12 shows an assessment of domestic co-product sulfur production and potential for 1974 and 2000 by seven types of sulfur sources. For 1974, it includes the actual production from these sources and the estimated potential capability for production. For 2000, it includes an estimate of the probable forecast production from an estimated potential capability for production.

Table X-10. SUMMARY OF FORECASTS OF U.S. AND REST-OF-WORLD SULFUR DEMAND, 1973-2000

Source: Ref. 99

(Thousand long tons)

	1973	2000 forecast range		Probable		Probable average annual growth rate 1973–2000 (percent)
		Low	High	1985	2000	
United States:						
Total	10,234	18,000	26,000	14,500	23,000	3.0
Cumulative	----	380,000	460,000	150,000	430,000	----
Rest of world:						
Total	32,766	72,000	104,000	50,500	87,000	3.7
Cumulative	----	1,400,000	1,700,000	500,000	1,500,000	----
World:						
Total	43,000	90,000	130,000	65,000	110,000	3.6
Cumulative	----	1,780,000	2,160,000	650,000	1,930,000	----

Table X-11. PROJECTIONS AND FORECASTS FOR U.S. SULFUR DEMAND BY END USE, 1973 and 2000

Source: Ref. 99

(Thousand long tons)

End use	1973	2000 Contingency forecasts for United States			
		Forecast base	Forecast range		Probable
			Low	High	
Agriculture (fertilizers)	5,520	12,300	9,400	14,300	12,300
Plastic and synthetic products	580	1,200	1,100	1,400	1,300
Paper products	370	500	300	600	400
Paints	420	----	----	----	----
Nonferrous metal production (Cu-U)	500	1,300	1,300	1,500	1,500
Explosives	280	700	400	600	500
Petroleum refining	230	600	500	600	500
Iron and steel production	110	----	----	----	----
Other	2,224	6,000	5,000	7,000	6,500
Total	10,234	----	18,000	26,000	23,000

Table X-12. CO-PRODUCT SULFUR PRODUCTION AND POTENTIAL FOR 1974 AND 2000

(Thousand long tons)

	1974		2000	
	Production	Potential capability	Forecast production	Potential capability
Coal	-	10,900	9,200	30,600
Petroleum	1,462	5,700	5,500	8,700
Natural Gas	1,218	1,280	1,100	1,120
Copper	552	1,870	3,550	3,930
Zinc	242	300	500	550
Lead	39	90	125	140
Other metal sulfurs	5	60	25	60
Total	3,518	20,200	20,000	45,100

Source Ref. 99

The forecast production for 2000 is based upon the ongoing development of the required technology for the production of marketable sulfur or sulfuric acid from the various sources, and environmental restraints that will enforce the production of these sulfur products regardless of normal economic considerations. During 1974, the co-product sulfur production was only 17% of the potential capability and ranged from nothing (in case of coal) to 95% (in the case of nature gas)[126] By 2000, it is forecast that this type of sulfur recovery will increase to 44% of the potential capability. It will range from 30% of the estimated potential capability for coal to 98% for natural gas. Coal is clearly indicated as being the principal source of co-product sulfur in 2000, accounting for 46% of the estimated forecast production, followed by petroleum with 27.5%.[127]

In 1974, coproduct sulfur production accounted for 31% of the production of sulfur in all forms and met 32% of U.S. demand.[128] By 2000, it is projected that co-product sulfur production will account for 83% of U.S. sulfur production in all forms and supply 87% of U.S. demand. With forecast domestic co-product sulfur production amount to 20 million tons per year by 2000, the remaining 3 million tons per year required to cover domestic requirements can be obtained as domestic native sulfur by the Frasch process, by imports of recovered elemental sulfur from Canada, and by importing Frasch sulfur from Mexico.

The foreseeable changes in the sources of future sulfur production have important implications that concern both producers and consumers. It will certainly change the existing marketing patterns and price structure to a point where they will be entirely different from what they are now. It is predicted that the net effect of these changes will be to break down the sulfur-producing and sulfur consuming industries into regional segments, each with its own supply-demand relationships that will be largely independent of other regions.

Westinform Service Ltd. (London) in a report entitled "Sulfur '85"[129] predicts an acute brimstone shortage of 8.8 million tons, almost 15% of the potential demand, by 1985 due to the inability of producers to match a rapid growth in world demand. They add that constraints on Canadian exports may cause this deficit to occur even earlier perhaps by the late 1970's or early 1980's. The world brimstone shortage by the regions for 1985 is given in Table X-13.

The tight brimstone supply conditions can be expected to give rise to a rapid increase in demand for imported sulfuric acid of smelter or pyritic origin, and/or the resurgence in the use of pyrites and hence trading in pyrites. It is predicted that sulfuric acid trading could increase from 1.5 million tons in 1976 to 2.1 million tons in 1980 and 6.3 million tons by 1985.

Table X-13. WORLD BRIMSTONE SHORTAGE BY REGIONS: 1985

	Volume (1000 tonnes)
West Europe	2608
East Europe	259
Africa	1140
Asia/Oceanic	1564
South America	939
North America	1984
Middle East	325
Total	8819

Source: Ref. 129

Cost and Pricing

Operating factors in the sulfur industry are diverse because of the widely differing manners in which marketable products are produced and sold. Basically, the industry is divided into two sectors. In one, the production of sulfur is the sole objective, as typified by the Frasch process; in the other, sulfur or sulfuric acid is recovered as a byproduct or coproduct, as in the case of the natural gas, petroleum, and nonferrous smelter industries.

The Frasch sector of the sulfur industry is based on the orderly exploitation of discreet deposits of native sulfur, with the objective of obtaining as nearly a complete recovery of the resource as economic conditions will permit. This requires an assured market and a stable, viable price structure that will be attractive to both producers and consumers. Under normal conditions, the assured market is based on the relatively close proximity of these deposits to the Nation's fertilizer production centers, and the availability of cheap water transportation to these points.

The major items of operating expense in Frasch production are the fuel for heating the process water, chemicals for treating (softening) the water, and the cost of drilling wells for extracting the sulfur. The major possible constraints to a sustained orderly development of the Frasch sector of industry would be a long period of depressed prices and a continued increase in fuel prices. This would restrict production to the higher grade sections of operating properties, and the lower grade ores probably would be lost.

The operating factors in the co-product sector of the industry are much more complex. This is because the sulfur revenues represent only a small portion of the revenues from the primary mineral production. In fact, the sulfur production may be enforced by the need to remove sulfur from the primary product so as to be able to market it or by environmental restraints on the release of sulfur compounds. Additionally, there may be no ready market for the sulfur or sulfuric acid that may be produced. Under these conditions, the economic desirability of producing sulfur may be subordinate to the necessity of producing it.

The major expense in the production of co-product sulfur is the amortization of the large capital expenditures required. Operating costs will range from low to medium, depending upon the type of feed to the recovery plants.

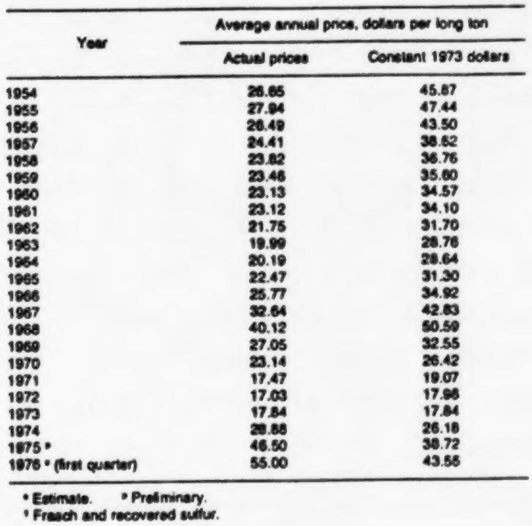
The U.S. Bureau of Mines in their Mineral Industry Survey gives the average net shipment value f.o.b. mine/plant for Frasch and recovered elemental sulfur of $45.63 per ton in 1975. The year-end price for Frasch sulfur was $65 per ton. There were corresponding increases in both export and import prices. The average sales value of shipment of Frasch sulfur f.l.b. mine for both domestic consumption and exports during 1975 rose to $50.16 per ton. The average price of recovered elemental sulfur was lower than Frasch sulfur. As a nondiscretionary byproduct, there was a general tendency for the industry to sell in local markets at prices that were competitively lower than sulfur from other sources. Prices varied widely in different regions of the nation as a resulf of these competitive factors. Reported unit shipment values of recovered sulfur f.o.b. plant in 1975 were $36.14 per ton. The time-price relationship for sulfur from 1954 to present is given in Table X-14.

The prices of sulfur and sulfuric acid as reported by the Chemical Marketing Reporter dated October 25, 1976,[130] are as follows:

- Sulfur crude, molten, f.o.b. vessels, Gulf port - $60-61/ton
- Canadian f.o.b., Alberta for U.S. delivery - $25/ton
- Dark sulfur, Ex-Tampa, Florida - $65-66/ton
- Sulfuric acid (100%)
  East Coast - $47.70-53.25/ton
  Gulf Coast - $44.95-50.25/ton
  West Coast - $49.75-55.30/ton
  Other areas - $32.60-53.40/ton

These prices are not firm indicators of actual prices paid, however, since discounts, variability in credit terms to buyers,

Table X-14. TIME-PRICE RELATIONSHIP FOR SULFUR



Year	Average annual price, dollars per long ton	
	Actual prices	Constant 1973 dollars
1954	26.65	45.87
1955	27.94	47.44
1956	26.49	43.50
1957	24.41	38.62
1958	23.82	36.76
1959	23.46	35.60
1960	23.13	34.57
1961	23.12	34.10
1962	21.75	31.70
1963	19.99	28.76
1964	20.19	28.64
1965	22.47	31.30
1966	25.77	34.92
1967	32.64	42.83
1968	40.12	50.59
1969	27.05	32.55
1970	23.14	26.42
1971	17.47	19.07
1972	17.03	17.96
1973	17.84	17.84
1974	28.88	26.18
1975 [a]	46.50	38.72
1976 [b] (first quarter)	55.00	43.56

[a] Estimate. [b] Preliminary.

[c] Frasch and recovered sulfur.

Source: Ref. 131

and service fees combine to determine the realized price available to the producer. Local situations can result in lower prices.

Sulfuric acid production has primarily been sited adjacent to the consuming industries it serves. Because of the high shipping costs relative to the price of sulfuric acid, most sulfuric acid is consumed within several hundred miles of the producing point. Only with the recent advent of regional inbalance in sulfuric acid supply and demand created due to the stringent air pollution regulations and high Frasch sulfur price, has more distant rail shipment and to some extent, ocean transport, became more important.

The selling price for acid can vary considerably depending upon the seller's situation and also the buyer's. In the case of the seller, if acid is being produced as a resulf of pollution control techniques then the quantity available for sale is dependent upon production of other products rather than the acid market. Thus if the seller can arrange for a long term (and usually low selling price) contract, he would prefer this rather than trying to change his customers depending upon the acid market price at any current time. As mentioned, the cost of shipping sulfuric acid is very high in proportion to the selling price and therefore, its shipping range is limited. Currently 500 to 1,000 miles is the maximum shipping range.

The smelters in the southwest of the United States are selling acid in the $8-15 per ton range. Long term contracts and/or increased acid availability could reduce this price. Smelter utility and refinery acid projected increase in supply seems to indicate reduced prices unless proposed market demand and/or Frasch sulfur prices change considerably.

APPENDIX Y

BACKGROUND MATERIAL, ASSUMPTIONS, AND CALCULATIONS FOR BLENDING SCENARIOS

Y-1 REVERBERATORY FURNACE SO_2 OFFGAS CHARACTERISTICS

Reverberatory SO_2 offgas concentrations fluctuate due to intermittent calcine charging. The amount of fluctuation varies from smelter to smelter depending on both age of smelter and local smelting practice. Since this report deals with a new smelting unit, it follows that many of the problems with older smelters will be eliminated, i.e., excess air dilution, large fluctuations, leaks, etc. As a result, the fluctuations will be minimized while SO_2 offgas strengths will be slightly increased.

With the above in mind, it was decided to choose an example smelter that has minimal fluctuations and higher SO_2 strengths to serve as a model for the RF offgases used in this study. The Onahama in Japan is representative since it was constructed relatively recently. Although they process green charge, the RF offgases were used to serve as a basis for the new smelter considered in this study. By using a green charge smelter, larger SO_2 fluctuations might be experienced than would be the case for a calcine charge RF. However, this tends to add conservatism for the SO_2 profile chosen for this study.

Figure Y-1 shows the actual SO_2 emissions from the Onahama smelter versus time. As can be seen, these fluctuations are not as great as some (see text, Figure 2-4).

Figure Y-2 shows a rough approximation of such emissions that were made so calculations could be carried out more efficiently.

The above figure (Y-2) was used to calculate emissions from the new smelter under consideration for this study. Since the adjusted Onahama's average SO_2 concentration is 2.5 percent, the average concentration chosen for this study (1 percent) was scaled down by a factor of 2.5 percent to be more representative of U.S. practice. The results are summarized in Table Y-1.

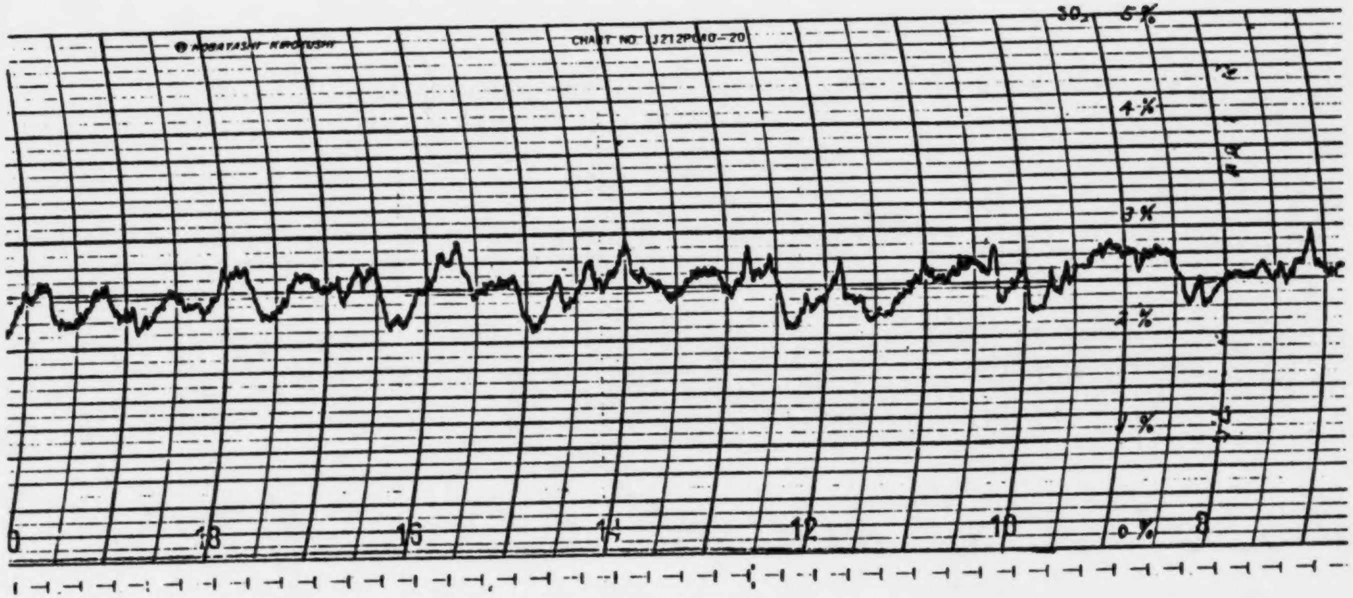


Figure Y-1. Percent SO_2 Emissions Versus Time From Onahama Reverberatory Furnace

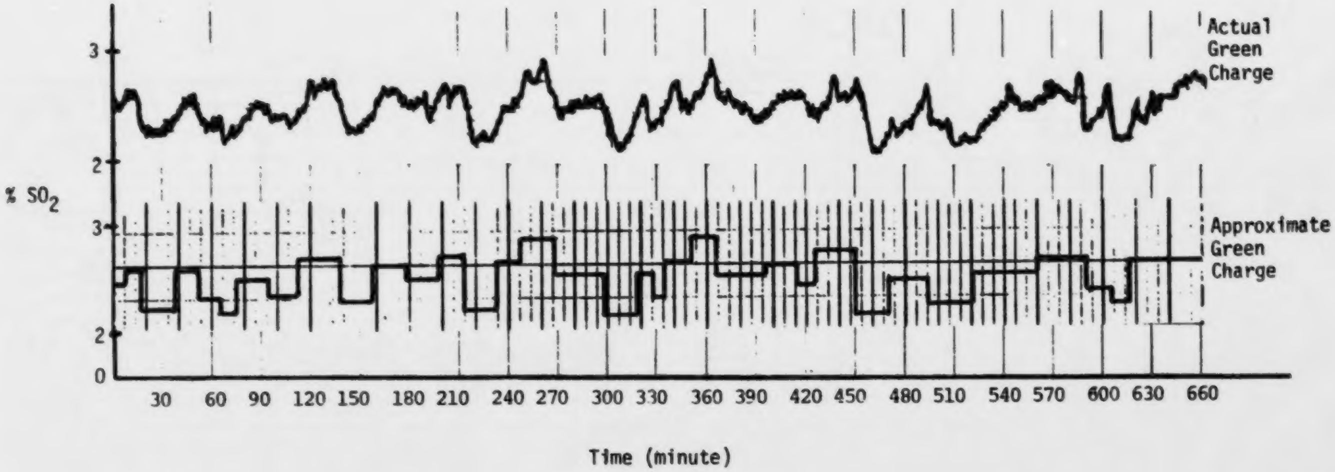


Figure Y-2. Reverberatory SO_2 Offgas Versus Time - Approximation

Table Y-1. REVERBERATORY OFFGAS SO_2 PROFILE

ONAHAMA				MODEL SMELTER USED			
Time (Minutes)	Percent SO_2	Time (Minutes)	Percent SO_2	Time (Minutes)	Percent SO_2	Time (Minutes)	Percent SO_2
7.5	2.46	30	2.50	7.5	0.98	30	1.0
10	2.58	20	2.61	10	1.03	20	1.04
20	2.23	10	2.42	20	0.89	10	0.97
15	2.58	25	2.73	15	1.03	25	1.09
12.5	2.31	20	2.15	12.5	0.92	20	0.86
10	2.19	25	2.46	10	0.88	25	0.98
20	2.5	25	2.23	20	1.0	25	0.89
17.5	2.35	40	2.50	17.5	0.94	40	1.0
25	2.69	30	2.65	25	1.08	30	1.06
20	2.27	15	2.38	20	0.91	15	0.95
20	2.62	10	2.23	20	1.05	10	0.89
20	2.5	45	2.62	20	1.00	45	1.05
15	2.69			15	1.08		
20	2.19			20	0.88		
15	2.65			15	1.06		
20	2.84			20	1.14		
30	2.53			30	1.01		
20	2.15			20	0.86		
10	2.53			10	1.01		
7.5	2.31			7.5	0.92		
15	2.65			15	1.06		
15	2.85			15	1.14		

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APPENDIX Y-2

CALCULATED GAS CHARACTERISTICS FOR ONE CONVERTER CYCLE (11 HOURS) FOR SCENARIOS HANDLING RF OFFGASES IN A FGD SYSTEM

Table Y-2. BLENDED: MHR + RF (O_2 ENRICH) + CONVERTERS

	Time (minutes)	Vol - SO_2	% O_2	Time (minutes)	Vol - SO_2	% O_2
1	5	217000-345	8.86	55	217000-345	8.85
2	2.5	177000-332	8.69	4.5	177000-330	8.59
3	10	177000-334	8.58	7.5	177600-330	8.62
4	2.5	177000-329	8.63	13	177000-335	8.57
5	11	137000-309	8.28	2	217000-347	8.84
6	6.5	177000-329	8.63	18	217000-349	8.82
7	7.5	177000-334	8.58	2	177600-337	8.55
8	7.5	217000-346	8.55	8	177000-333	8.59
9	12.5	217000-343	8.87	11	137000-313	8.18
10	10	217000-342	8.88	11	177000-332	8.59
11	10	217000-345	8.85	3	177000-334	8.58
12	10	177000-333	8.59	5	219000-425	11.42
13	15	137000-311	8.21	12	179000-413	10.57
14	2.5	177000-331	8.61	8	179000-410	10.59
15	6.5	177000-335	8.57	2	219000-423	11.43
16	10	217000-347	8.83	8	219000-426	11.40
17	5.5	177000-335	8.57	17	179000-414	10.55
18	11.5	177000-330	8.62	8	179000-407	10.62
19	5	137000-310	8.22	5	219000-420	11.46
20	3.5	177000-330	8.62	7	177000-328	8.64
21	3.5	177000-334	8.58	9	177000-332	8.60
22	10	137000-315	8.16	14	137000-312	8.19
23	5	179000-395	9.22	2	177000-332	8.60
24	1.5	179000-413	10.56	13	177000-329	8.63
25	7.5	179000-411	10.58	9	217000-342	8.88
26	11.5	219000-424	11.43	8	177000-329	8.63
27	8.5	219000-426	11.41	23	177000-333	8.59
28	6.5	179000-414	10.55	17	217000-345	8.85
29	20	179000-408	10.61	2	217000-347	8.84
30	2.5	179000-413	10.56	5	177000-335	8.57
31	5	219000-425	11.41	19	137000-316	8.16
32	5	217000-347	8.84	4	177000-335	8.57
33	2.5	177000-335	8.57	1	177000-331	8.61
34	1.5	177000-337	8.55	5	217000-344	8.86
35	17.5	137000-319	8.13	9	219000-422	11.44
36	5.5	137000-314	8.18	10	219000-424	11.45
37	15	217000-345	8.85	10	219000-425	11.41
38	7.5	177000-333	8.59	20	179000-413	10.56
39	15.5	177000-328	8.64	10	179000-395	9.22
40	4.5	217000-342	8.89	5	179000-413	10.56

Table Y-2. BLENDED: MHR + RF (O_2 ENRICH) + CONVERTERS

	Time (minutes)	Vol - SO_2	% O_2	Time (minutes)	Vol - SO_2	% O_2
1	5	203896-367	9.11	55	203896-368	9.10
2	2.5	163896-359	8.89	4.5	163896-360	8.88
3	10	163896-360	8.87	7.5	163896-357	8.91
4	2.5	163896-356	8.92	13	163896-361	8.86
5	11	123896-341	8.57	2	203896-369	9.09
6	6.5	163896-356	8.92	13	203896-371	9.06
7	7.5	163896-360	8.87	2	163896-364	8.83
8	7.5	203896-360	9.09	8	163896-359	8.88
9	12.5	203896-365	9.12	11	123896-346	8.52
10	10	203896-364	9.14	11	163896-359	8.88
11	10	203896-367	9.10	3	163896-361	8.87
12	10	163896-359	8.88	5	205896-452	11.82
13	15	123896-344	8.55	12	165896-445	11.01
14	2.5	163896-357	8.90	8	165896-443	11.03
15	6.5	163896-362	8.86	2	205896-450	11.89
16	10	203896-370	9.08	6	205896-453	11.81
17	8.5	163896-362	8.86	17	165896-447	10.99
18	11.5	163896-356	8.92	8	165896-439	11.07
19	5	123896-342	8.57	5	205896-447	11.88
20	3.5	163896-356	8.92	7	163896-356	8.93
21	3.5	163896-361	8.87	9	163896-359	8.89
22	10	123896-349	8.50	14	123896-345	8.53
23	5	125896-436	9.66	8	163896-359	8.89
24	1.5	165896-446	11.00	13	163896-356	8.92
25	8.5	165896-444	11.02	9	203896-364	9.13
26	11.5	205896-451	11.84	8	163896-356	8.92
27	8.5	205896-453	11.81	23	163896-359	8.88
28	6.5	165896-447	10.99	17	203896-367	9.10
29	20	165896-440	11.06	2	203896-369	9.09
30	2.5	165896-446	11.00	5	163896-361	8.86
31	5	205896-452	11.82	19	123896-349	8.50
32	5	203896-369	9.09	4	163896-361	8.86
33	2.5	163896-361	8.86	1	163896-358	8.90
34	1.5	163896-364	8.83	5	203896-366	9.12
35	17.5	123896-353	8.46	9	205896-449	11.85
36	5.5	123896-347	8.52	10	205896-448	11.87
37	15	203896-368	9.10	10	205896-452	11.82
38	8.5	163896-360	8.88	20	165896-446	11.00
39	15.5	163896-354	8.93	10	125896-436	9.66
40	4.5	203896-363	9.14	5	165896-446	11.00

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Table Y-3. BLENDED: MHR + CONVERTERS

	Time (minutes)	Vol - SO_2	% O_2	Time (minutes)	Vol - SO_2	% O_2
1	5	163000-426	10.79	5	123000-4.35	11.05
2	15	123000-435	11.05	19	83000-452	11.55
3	11	83000-452	11.55	5	123000-435	11.05
4	14	123000-435	11.05	5	163000-426	10.79
5	40	163000-426	10.79	29	165000-530	14.18
6	10	123000-435	11.05	20	125000-546	13.85
7	15	83000-452	11.55	10	85000-579	13.20
8	9	123000-435	11.05	5	125000-546	13.85
9	10	163000-426	10.79			
10	20	123000-435	11.05			
11	5	83000-452	11.55			
12	7	123000-435	11.05			
13	10	83000-452	11.55			
14	5	85000-579	13.20			
15	10	125000-546	13.85			
16	20	165000-530	14.18			
17	29	125000-546	13.85			
18	5	165000-530	14.18			
19	5	163000-426	10.79			
20	4	123000-435	11.05			
21	24	83000-452	11.55			
22	15	163000-426	10.79			
23	25	123000-435	11.05			
24	10	163000-426	10.79			
25	25	123000-435	11.05			
26	15	163000-426	10.79			
27	10	123000-435	11.05			
28	11	83000-452	11.55			
29	14	123000-435	11.05			
30	5	165000-530	14.18			
31	20	125000-546	13.55			
32	10	165000-530	14.18			
33	25	125000-546	13.55			
34	5	165000-530	14.18			
35	16	123000-435	11.05			
36	14	83000-452	11.55			
37	15	123000-435	11.05			
38	9	163000-426	10.79			
39	26	123000-435	11.55			
40	19	163000-426	10.79			

Table Y-4. BLENDED: (MHR + CONVERTERS) + (RF ——→ MgO SYSTEM)

	Time (minutes)	Vol - SO_2	% O_2	Time (minutes)	Vol - SO_2	% O_2
1	5	167860-443	10.71	5	127860-456	10.43
2	15	127860-456	10.93	19	87860-482	11.35
3	11	87860-482	11.35	5	127860-456	10.93
4	14	127860-456	10.93	5	167860-443	10.71
5	10	167860-443	10.71	29	169860-543	14.00
6	10	127860-456	10.93	20	129860-563	19.13
7	15	87860-482	11.35	10	89860-602	12.92
8	9	127860-456	10.93	5	129860-563	13.63
9	10	167860-443	10.71			
10	20	127860-456	10.93			
11	5	87860-482	11.35			
12	7	127860-456	10.93			
13	10	87860-482	11.35			
14	5	89860-602	12.92			
15	10	129860-563	13.63			
16	20	169860-543	14.00			
17	29	129860-563	13.63			
18	5	169860-543	14.00			
19	5	167860-443	10.71			
20	4	127860-456	10.93			
21	24	87860-482	11.35			
22	15	167860-443	10.71			
23	25	127860-456	10.93			
24	10	167860-443	10.71			
25	25	127860-456	10.93			
26	15	167860-443	10.71			
27	10	127860-456	10.93			
28	11	87860-482	11.35			
29	14	127860-456	10.93			
30	5	169860-543	14.00			
31	20	129860-563	13.63			
32	10	169860-543	14.00			
33	25	129860-563	13.63			
34	5	169860-543	14.00			
35	16	127860-456	10.93			
36	14	87860-482	11.35			
37	15	127860-456	10.93			
38	9	167860-443	10.71			
39	26	127860-456	10.93			
40	19	167860-443	10.71			

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Table Y-5. BLENDED: (MHR + CONVERTER)+(RF ——→ CITRATE SYSTEM)

	Time (minutes)	Vol - SO_2	% O_2	Time (minutes)	Vol - SO_2	% O_2
1	5	163510-454	10.76	5	123510-472	11.00
2	15	123510-472	11.00	19	83510-507	11.50
3	11	83510-507	11.50	5	123510-472	11.00
4	14	123510-472	11.00	5	163510-454	10.76
5	40	163510-454	10.76	29	165510-558	14.14
6	10	123510-472	11.00	20	125510-582	13.79
7	15	83510 507	11.50	10	5510-632	13.12
8	9	123510-472	11.00	5	125510-582	13.79
9	10	163510-454	10.76			
10	20	123510-472	11.00			
11	5	83510-507	11.50			
12	7	123510-472	11.00			
13	10	83510-507	11.50			
14	5	85510-632	13.12			
15	10	125510-582	13.79			
16	20	165510-558	14.14			
17	29	125510-582	13.79			
18	5	16550-558	14.14			
19	5	163510-454	10.76			
20	4	123510-472	11.00			
21	24	83510-507	11.50			
22	15	163510-454	10.76			
23	25	123510-472	11.00			
24	10	163510-454	10.76			
25	25	123510-472	11.00			
26	15	163510-454	10.76			
27	10	123510-472	11.00			
28	11	83510-507	11.50			
29	14	123510-472	11.00			
30	5	165510-558	14.14			
31	20	125510-582	13.79			
32	10	165510-558	14.14			
33	25	125510-582	13.79			
34	5	165510-558	14.14			
35	16	12350-472	11.00			
36	14	83510-507	11.50			
37	15	123510-472	11.00			
38	9	163510-454	10.76			
39	26	123510-472	11.00			
40	19	163510-454	10.76			

Table Y-6. BLENDED: (MHR + CONVERTER) WHEN RF HAS O_2 ENRICHMENT

	Time (minutes)	Vol - SO_2	% O_2	Time (minutes)	Vol - SO_2	% SO_2
1	5	162096-426	10.78	5	122096-434	11.03
2	15	122096-434	11.03	19	82096-451	11.53
3	11	82096-451	11.53	5	122096-434	11.03
4	14	122096-434	11.03	5	162096-426	10.78
5	40	162096-426	10.78	29	164096-530	14.19
6	10	122096-434	11.03	20	124096-546	13.86
7	15	82096-451	11.53	10	84096-580	13.20
8	9	122096-434	11.03	5	124096-546	13.86
9	10	162096-426	10.78			
10	20	122096-434	11.03			
11	5	82096-451	11.53			
12	7	122096-434	11.03			
13	10	82096-451	11.53			
14	5	84096-580	13.20			
15	10	124096-546	13.86			
16	20	164096-530	14.19			
17	29	124096-546	13.86			
18	5	164096-530	14.19			
19	5	162096-426	10.78			
20	4	122096-434	11.03			
21	24	82096-451	11.53			
22	15	162096-426	10.78			
23	25	122096-434	11.03			
24	10	162096-426	10.78			
25	25	122096-434	11.03			
26	15	162096-426	10.78			
27	10	122096-434	11.03			
28	11	82096-451	11.53			
29	14	122096-434	11.03			
30	5	164096-530	14.19			
31	20	124096-546	13.86			
32	10	164096-530	14.19			
33	25	124096-546	13.86			
34	5	164096-530	14.19			
35	16	122096-434	11.03			
36	14	82096-451	11.53			
37	15	122096-434	11.03			
38	9	162096-426	10.78			
39	26	122096-434	11.03			
40	19	162096-426	10.78			

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Table Y-7. BLENDED: (MHR + CONVERTER)+[O_2 ENRICHMENT) ⟶ MgO SYSTEM]

	Time (minutes)	Vol - SO_2	% O_2	Time (minutes)	Vol - SO_2	% O_2
1	5	167366-444	10.69	5	127366-457	10.90
2	15	127366-457	10.90	19	87366-484	11.32
3	11	87366-484	11.32	5	127366-457	10.90
4	14	127366-457	10.90	5	167366-444	10.69
5	40	167366-444	10.69	29	169366-545	14.00
6	10	127366-457	10.90	20	129366-564	13.62
7	15	87366-484	11.32	10	89366-605	12.89
8	9	127366-457	10.90	5	129366-564	13.62
9	10	167366-444	10.69			
10	20	127366-457	10.90			
11	5	87366-484	11.32			
12	7	127366-457	10.90			
13	10	87366-484	11.32			
14	5	89366-605	12.89			
15	10	129366-564	13.62			
16	20	167366-545	14.00			
17	29	129366-564	13.62			
18	5	169366-545	14.00			
19	5	167366-444	10.69			
20	4	127366-457	10.90			
21	24	87366-484	11.32			
22	15	167366-444	10.69			
23	25	127366-457	10.90			
24	10	167366-444	10.69			
25	25	127366-457	10.90			
26	15	167366-444	10.69			
27	10	127366-457	10.90			
28	11	87366-484	11.32			
29	14	127366-457	10.90			
30	5	169366-545	14.00			
31	20	129366-564	13.62			
32	10	169366-545	14.00			
33	25	129366-564	13.62			
34	5	169366-545	14.00			
35	16	127366-457	10.90			
36	14	87366-484	11.32			
37	15	127366-457	10.50			
38	9	167366-444	10.69			
39	26	127366-457	10.90			
40	19	167366-444	10.69			

TABLE Y-8. BLENDED: (MHR + CONVERTER)+[O_2 ENRICHMENT) → CITRATE SYSTEM]

	Time (minutes)	Vol - SO_2	% O_2	Time (minutes)	Vol - SO_2	% O_2
1	5	162646-457	10.74	5	122646-475	10.95
2	15	122646-475	10.98	19	82646-511	11.45
3	11	82646-511	11.45	5	122646-475	10.98
4	14	122646-475	10.98	5	162646-457	10.74
5	40	162646-457	10.74	29	164646-560	14.14
6	10	122646-475	10.98	20	124646-586	13.80
7	15	82646-511	11.45	10	84646-638	13.11
8	9	122646-475	10.98	5	124646-586	13.50
9	10	162646-457	10.74			
10	20	122646-475	10.98			
11	5	82646-511	11.45			
12	7	122646-475	10.98			
13	10	82646-511	11.45			
14	5	84646-638	13.11			
15	10	124646-586	13.80			
16	20	164646-560	14.14			
17	29	124646-586	13.80			
18	5	164646-560	14.14			
19	5	162646-457	10.74			
20	4	122646-475	10.98			
21	24	82646-511	11.45			
22	15	162646-457	10.74			
23	25	122646-475	10.98			
24	10	162646-457	10.74			
25	25	122646-475	10.94			
26	15	162646-457	10.74			
27	10	122646-475	10.98			
28	11	82646-511	11.45			
29	14	122646-475	10.98			
30	5	164646-560	14.14			
31	20	124646-586	13.80			
32	10	164646-560	14.14			
33	25	124646-586	13.80			
34	5	164646-560	14.14			
35	16	122646-475	10.98			
36	14	82646-511	11.45			
37	15	122646-475	10.98			
38	9	162646-457	10.74			
39	26	122646-475	10.98			
40	19	162646-457	10.74			

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Table Y-9 . BLENDED: FBR + RF + CONVERTERS

	Time (minutes)	Vol - SO_2	% O_2	Time (minutes)	Vol - SO_2	% O_2
1	5	197600-378	7.38	5.5	197600-379	7.37
2	2.5	157600-373	6.71	4.5	157600-374	6.70
3	10	157600-375	6.69	7.5	157600-371	6.73
4	2.5	157600-370	6.74	13	157600-376	6.65
5	11	117600-360	5.63	2	197600-381	7.35
6	6.5	157600-376	6.74	13	197600-383	7.33
7	7.5	157600-375	6.69	2	157600-378	6.66
8	7.5	197600-380	7.36	8	157600-374	6.70
9	12.5	197600-377	7.39	11	117600-365	5.58
10	10	197600-376	7.40	11	157600-374	6.70
11	10	197600-379	7.37	3	157600-375	6.69
12	10	157600-374	6.70	5	199600-466	10.20
13	15	117600-362	5.61	12	159600-463	8.94
14	2.5	157600-372	6.72	8	159600-460	8.96
15	6.5	157600-376	6.68	2	199600-464	10.22
16	10	197600-381	7.35	5	199600-467	10.18
17	8.5	157600-376	6.65	17	159600-464	8.92
18	11.5	157600-370	6.73	8	159600-457	9.00
19	5	117600-360	5.62	5	199600-461	10.25
20	3.5	157600-370	6.73	7	157600-369	6.75
21	3.5	157600-375	6.69	9	157600-373	6.71
22	10	117600-367	5.56	14	117600-364	5.59
23	5	119600-459	6.83	2	157600-373	6.71
24	1.5	159600-463	8.94	13	157600-370	6.74
25	8.5	159600-461	8.95	9	197600-376	7.40
26	11.5	199600-465	10.21	3	157600-370	6.74
27	8.5	199600-467	10.19	23	157600-374	6.70
28	6.5	159600-469	8.93	17	197600-379	7.37
29	20	159600-457	8.99	2	197600-381	7.35
30	2.5	159600-463	8.93	5	157600-376	6.68
31	5	199600-466	10.19	19	117600-367	5.55
32	5	197600-381	7.35	4	157600-376	6.66
33	2.5	157600-376	6.68	1	157600-372	6.72
34	1.5	157600-378	6.66	5	197600-378	7.38
35	17.5	117600-371	5.52	9	199600-463	10.22
36	5.5	117600-365	5.58	10	199600-462	10.24
37	15	197600-379	7.37	10	199600-466	10.19
38	9.5	157600-374	6.70	20	159600-463	8.94
39	15.5	157600-369	6.75	10	119600-459	6.83
40	4.5	197600-375	7.41	5	199600-463	8.94

Table Y-10. BLENDED: FBR + (O_2 ENRICHMENT) + CONVERTER

	Time (minutes)	Vol - SO_2	% O_2	Time (minutes)	Vol - SO_2	% O_2
1	5	184900-404	7.58	5.5	184900-405	7.58
2	2.5	144900-405	6.92	4.5	144900-407	6.91
3	10	144900-407	6.90	7.5	144900-403	6.94
4	2.5	144900-402	6.95	13	144900-409	6.89
5	11	104900-403	5.79	2	184900-407	7.56
6	6.5	144900-402	6.95	13	184900-409	7.53
7	7.5	144900-407	6.90	2	144900-412	6.85
8	7.5	184900-406	7.57	8	144900-406	6.91
9	12.5	184900-402	7.60	11	104900-409	5.73
10	10	184900-401	7.62	11	144900-406	6.91
11	10	184900-405	7.58	3	144900-405	6.89
12	10	144900-406	6.91	5	184900-498	10.59
13	15	104900-406	5.76	12	144900-503	9.33
14	2.5	144900-404	6.93	8	144900-500	9.36
15	6.5	144900-404	6.85	2	184900-495	10.62
16	10	184900-407	7.55	8	184900-499	10.58
17	8.5	144900-409	6.85	17	144900-505	9.31
18	11.5	144900-403	6.95	8	144900-495	9.41
19	5	104900-404	5.78	5	184900-492	10.65
20	3.5	144900-403	6.95	7	144900-401	6.97
21	3.5	144900-408	6.89	9	144900-405	6.92
22	10	104900-411	5.70	14	104900-408	5.74
23	5	104900-513	7.12	8	144900-405	6.92
24	1.5	144900-503	9.33	13	144900-402	6.95
25	8.5	144900-501	9.35	9	184900-402	7.61
26	11.5	184900-496	10.61	8	144900-402	6.95
27	8.5	184900-499	10.58	23	144900-406	6.91
28	6.5	144900-504	9.32	17	184900-405	7.58
29	20	144900-496	9.40	2	184900-407	7.56
30	2.5	144900-503	9.33	5	144900-409	6.89
31	5	184900-498	10.59	19	104900-412	5.70
32	5	184900-407	7.56	4	144900-409	6.89
33	2.5	144900-409	6.89	1	144900-404	6.93
34	1.5	144900-412	6.85	5	184900-403	7.59
35	17.5	104900-417	5.65	9	186900-495	10.62
36	5.5	104900-409	5.72	10	184900-493	10.64
37	15	184900-405	7.58	10	184900-498	10.59
38	9.5	144900-407	6.91	20	144900-503	9.33
39	15.5	144900-401	6.97	10	106900-513	7.12
40	4.5	184900-400	7.62	5	146900-503	9.33

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Table Y-11. BLENDED: FBR + CONVERTER

	Time (minutes)	Vol - SO_2	% O_2	Time (minutes)	Vol - SO_2	% O_2
1	5	143600-4.84	9.01	5	103600-5.16	8.63
2	15	103600-5.16	8.63	19	63600-5.89	7.77
3	11	63600-5.89	7.77	5	103600-5.16	8.63
4	14	103600-5.16	8.63	5	143600-4.84	9.01
5	40	143600-4.84	9.01	29	145600-6.00	12.88
6	10	103600-5.16	8.63	20	105600-6.46	12.00
7	15	63600-5.89	7.77	10	65600-7.50	10.02
8	9	103600-5.16	8.63	5	105600-6.46	12.00
9	10	143600-4.84	9.01			
10	20	103600-5.16	8.63			
11	5	63600-5.89	7.77			
12	7	103600-5.16	8.63			
13	10	63600-5.89	7.77			
14	5	65600-7.50	10.02			
15	10	105600-6.46	12.00			
16	20	145600-6.00	12.88			
17	29	105600-6.46	12.00			
18	5	145600-6.00	12.88			
19	5	143600-4.84	9.01			
20	4	103600-5.16	8.63			
21	24	63600-5.89	7.77			
22	15	143600-4.84	9.01			
23	25	103600-5.16	8.63			
24	10	143600-4.84	9.01			
25	25	103600-5.16	8.63			
26	15	143600-4.84	9.01			
27	10	103600-5.16	8.63			
28	11	63600-5.89	7.77			
29	14	103600-5.16	8.63			
30	5	145600-6.00	12.88			
31	20	105600-6.46	12.00			
32	10	145600-6.00	12.88			
33	25	105600-6.46	12.00			
34	15	145600-6.00	12.88			
35	16	103600-5.16	8.63			
36	14	63600-5.89	7.77			
37	15	103600-5.16	8.63			
38	9	143600-4.84	9.01			
39	26	103600-5.16	8.63			
40	19	143600-4.84	9.01			

Table Y-12. BLENDED: (FBR + CONVERTER)+(RF ——► MgO SYSTEM)

	Time (minutes)	Vol - SO_2	% O_2	Time (minutes)	Vol - SO_2	% O_2
1	5	145460-5.01	8.98	5	108460-538	8.60
2	15	108460-538	8.60	19	68460-618	7.79
3	11	68460-618	7.79	5	108460-538	8.60
4	14	108460-538	8.60	5	145460-501	8.98
5	40	145460-501	8.98	29	150460-613	12.72
6	10	108460-538	8.60	20	112460-662	11.82
7	15	68460-618	7.79	10	70460-767	9.88
8	9	105460-538	8.60	5	110460-662	11.82
9	10	145460-501	8.98			
10	20	108460-538	8.60			
11	5	68460-618	7.79			
12	7	105460-538	8.60			
13	10	68460-618	7.79			
14	5	70460-767	9.88			
15	10	110460-662	11.82			
16	20	150460-613	12.72			
17	29	110460-662	11.82			
18	5	150460-613	12.72			
19	5	148460-501	8.98			
20	4	108460-538	8.60			
21	24	68460-618	7.79			
22	15	148460-501	8.98			
23	25	108460-538	8.60			
24	10	148460-501	8.98			
25	25	108460-538	8.60			
26	15	148460-501	8.98			
27	10	108460-538	8.60			
28	11	68460- 18	7.79			
29	14	108460-538	8.60			
30	5	150460-613	12.72			
31	20	110460-662	11.82			
32	10	150460-613	12.72			
33	25	110460-662	11.82			
34	5	150460-613	12.82			
35	16	108460-538	8.60			
36	14	68460-618	7.79			
37	15	105460-538	8.60			
38	9	145460-501	8.98			
39	26	105460-538	8.60			
40	19	145460-501	8.98			

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Table Y-13. BLENDED: (FBR + CONVERTER) + (RF ⟶ CITRATE SYSTEM)

	Time (minutes)	Vol - SO_2	% O_2	Time (minutes)	Vol - SO_2	% O_2
1	5	144110-516	8.98	5	104110-560	8.59
2	15	104110-560	8.59	19	64110-660	7.71
3	11	64110-660	7.71	5	104110-560	8.59
4	14	104110-560	8.59	5	144110-516	8.98
5	40	144110-516	8.98	29	146110-631	12.84
6	10	104110-560	8.59	20	106110-659	11.94
7	15	64110-660	7.71	10	66110-818	9.94
8	9	104110-560	8.59	5	106110-659	11.94
9	10	144110-516	8.98			
10	20	104110-560	8.59			
11	5	64110-660	7.71			
12	7	104110-560	8.59			
13	10	64110-660	7.71			
14	5	66110-818	9.44			
15	10	106110-659	11.94			
16	20	146110-631	12.84			
17	29	106110-659	11.94			
18	5	146110-631	12.84			
19	5	144110-516	8.98			
20	4	104110-560	8.59			
21	24	64110-660	7.71			
22	15	144110-516	8.98			
23	25	104110-560	8.59			
24	10	144110-516	8.98			
25	25	104110-560	8.59			
26	15	144110-516	8.98			
27	10	104110-560	8.59			
28	11	64110-660	7.71			
29	14	104110-560	8.59			
30	5	146110-631	12.84			
31	20	106110-659	11.94			
32	10	146110-631	12.84			
33	25	106110-659	11.94			
34	5	146110-631	12.84			
35	16	104110-560	8.59			
36	14	64110-660	7.71			
37	15	104110-560	8.59			
38	9	144110-516	8.98			
39	26	104110-560	8.59			
40	19	144110-516	8.98			

Table Y-14. BLENDED: (FBR + CONVERTER - ADJUSTED FOR RF 02 ENRICHMENT)

	Time (minutes)	Vol - SO_2	% O_2	Time (minutes)	Vol - SO_2	% O_2
1	5	143100-482	9.03	5	103100-514	8.66
2	15	103100-514	8.66	19	63100-587	7.80
3	11	63100-587	7.80	5	103100-514	8.66
4	14	63100-514	8.66	5	143100-482	9.03
5	40	143100-482	9.03	29	145100-599	12.91
6	10	103100-514	8.66	20	105100-645	12.04
7	15	63100-587	7.80	10	65100-749	10.06
8	9	103100-514	8.66	5	105100-645	12.04
9	10	143100-482	9.03			
10	20	103100-514	8.66			
11	5	63100-587	7.80			
12	7	103100-514	8.66			
13	10	63100-587	7.80			
14	5	65100-749	10.06			
15	10	105100-645	12.04			
16	20	145100-599	12.91			
17	29	105100-645	12.04			
18	5	145100-599	12.91			
19	5	143100-482	9.03			
20	4	103100-514	8.66			
21	24	63100-587	7.80			
22	15	143100-482	9.03			
23	25	103100-514	8.66			
24	10	143100-482	9.03			
25	25	103100-514	8.66			
26	15	143100-482	9.03			
27	10	103100-514	8.66			
28	11	63100-587	7.80			
29	14	103100-514	8.66			
30	5	145100-599	12.91			
31	20	105100-645	12.04			
32	10	145100-599	12.91			
33	25	105100-645	12.04			
34	5	145100-599	12.91			
35	16	103100-514	8.66			
36	14	63100-587	7.80			
37	15	103100-514	8.66			
38	9	143100-482	9.03			
39	26	103100-514	8.66			
40	19	143100-482	9.03			

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Table Y-15. BLENDED: (FBR + CONVERTER)+(FR(O_2 ENRICHMENT)⟶MgO SYSTEM)

	Time (minutes)	Vol - SO_2	% O_2	Time (minutes)	Vol - SO_2	% O_2
1	5	148370-500	8.99	5	108370-535	8.63
2	15	108370-538	8.63	19	68370-619	7.82
3	11	68370-619	7.82	5	108370-535	8.63
4	14	108370-538	8.63	5	148370-500	8.99
5	40	148370-500	8.99	29	150370-613	12.74
6	10	108370-538	8.63	20	110370-662	11.85
7	15	68370-619	7.82	10	70370-768	9.91
8	9	108370-538	8.63	5	110370-662	11.85
9	10	148370-500	8.99			
10	20	108370-533	8.63			
11	5	68370-619	7.82			
12	7	108370-538	8.63			
13	10	68370-619	7.82			
14	5	70370-768	9.91			
15	10	110370-662	11.85			
16	20	150370-613	12.74			
17	29	110370-662	11.85			
18	5	150370-613	12.74			
19	5	148370-500	8.99			
20	4	108370-538	8.63			
21	24	68370-619	7.82			
22	15	148370-500	8.99			
23	25	108370-538	8.63			
24	10	148370-500	8.99			
25	25	108370-538	8.63			
26	15	148370-500	8.99			
27	10	108370-538	8.63			
28	11	68370-619	7.82			
29	14	108370-538	8.63			
30	5	150370-613	12.74			
31	20	110370-662	11.85			
32	10	150370-613	12.74			
33	25	110370-662	11.85			
34	5	150370-613	12.74			
35	16	108370-535	8.63			
36	14	68370-619	7.82			
37	15	108370-538	8.63			
38	9	148370-500	8.99			
39	26	108370-539	8.63			
40	19	148370-500	8.99			

Table Y-16. BLENDED: (FBR + CONVERTER)+[O_2 ENRICHMENT ⟶ CITRATE SYSTEM]

	Time (minutes)	Vol - SO_2	% O_2	Time (minutes)	Vol - SO_2	% O_2
1	5	143650-517	9.00	5	103650-562	8.61
2	15	103650-562	8.61	18	63650-664	7.73
3	11	63650-664	7.73	5	103650-562	8.61
4	14	103650-562	8.61	5	143650-517	9.00
5	40	143650-517	9.00	29	145650-633	12.86
6	10	103650-562	8.61	20	105650-691	11.98
7	15	63650-664	7.73	10	65650-822	9.98
8	9	103650-562	8.61	5	105650-691	11.98
9	10	143650-517	9.00			
10	20	103650-562	8.61			
11	5	63650-664	7.73			
12	7	103650-562	8.61			
13	10	63650-664	7.73			
14	5	65650-822	9.98			
15	10	105650-691	11.98			
16	20	145650-633	12.86			
17	29	105650-691	11.98			
18	5	145650-633	12.86			
19	5	143650-517	9.00			
20	4	103650-562	8.61			
21	24	63650-664	7.73			
22	15	143650-517	9.00			
23	25	103650-562	8.61			
24	10	143650-517	9.00			
25	25	103650-562	8.61			
26	15	143650-517	9.00			
27	10	103650-562	8.61			
28	11	63650-664	7.73			
29	14	103650-562	8.61			
30	5	145650-633	12.86			
31	20	105650-691	11.98			
32	10	145650-633	12.86			
33	25	105650-691	11.98			
34	5	145650-633	12.86			
35	10	103650-562	8.61			
36	14	63650-665	7.73			
37	15	103650-562	8.61			
38	9	143650-517	9.00			
39	26	103650-562	8.61			
40	19	143650-517	9.00			

APPENDIX Y-3

ASSUMPTIONS FOR BLENDING SCENARIOS (TABLE 6-4 IN TEXT)

SUMMARY OF ASSUMPTIONS FOR TABLE 6-4 IN TEXT

A. BACKGROUND

1. SO_2 offgas concentrations are constant for multihearth roasters (MHR) and fluid-bed roasters (FBR)
2. Offgas volumes are constant for reverberatory furnace (RF), MHR, and FBR
3. Offgas volumes and SO_2 concentrations fluctuate for converters. Also SO_2 concentrations fluctuate for RF.
4. FGD concentration systems are assumed to be able to process fluctuating offgas volumes and SO_2 concentration and to produce an enriched offgas of constant volume and SO_2 concentration (FGD system design based on maximum volume input). Thus, the offgas volume and SO_2 concentration from the FGD system will be based on the average offgas volume and SO_2 concentration processed in such a system. Such offgas characteristics will be based on an assumed 95 percent SO_2 and 10 percent SO_2 for the citrate and magnesium oxide (MgO) system, respectively. The corresponding FGD concentrated SO_2 product volume will be calculated by:

$$A\,(B)\,\frac{.9}{C} = \text{Volume}$$

Where

A = Average volume of gas processed

B = Average percent SO_2 in A

C = FGD SO_2 offgas percent, and 0.9 = 90 percent efficient

B. VALUES USED FOR THE VARIOUS BLENDING STREAMS BASED ON BACKGROUND INFORMATION

	MAXIMUM		MINIMUM		AVERAGE	
Equipment	% SO_2	@ SCFM	% SO_2	@ SCFM	% SO_2	@ SCFM
1. No FGD Control: No Reverb O_2 enrichment						
Reverb Furnace	1.14	54,000	0.86	54,000	1.0	54,000
MHR	5.0	43,000	5.0	43,000	5.0	43,000
Converter	5.4	122,000	4.0	40,000	4.5	82,000
Fluid Bed Roaster	9.1	23,600	9.1	23,600	9.1	23,600
2. No FGD Control: Reverb O_2 Enrichment						
Reverb Furnace	1.6	41,800	1.2	41,800	1.4	41,800
MHR	5.0	42,096	5.0	42,096	5.0	42,096
Converter	5.4	122,000	4.0	40,000	4.5	82,000
Fluid Bed Roaster	9.1	23,100	9.1	23,100	9.1	23,100
3. MgO System: No O_2 Enrichment						
Reverb Furnace	10.0	5,540.4	10.0	4,179.6	10.0	4,860
MHR	10.0	19,350	10.0	19,350	10.0	19,350
Converter	10.0	59,292	10.0	14,400	10.0	33,210
Fluid Bed Roaster	10.0	19,328.4	10.0	19,328.4	10.0	19,328.4
4. MgO System: O_2 Enrichment						
Reverb Furnace	10.0	6,019.2	10.0	4,514.4	10.0	5,266.8
MHR	10.0	18,943.2	10.0	18,943.2	10.0	18,943.2
Converter	10.0	59,292	10.0	14,400	10.0	33,210
Fluid Bed Roaster	10.0	18,918.9	10.0	18,918.9	10.0	18,918.9
5. Citrate System: No O_2 Enrichment						
Reverb Furnace	95.0	583.2	95.0	430.48	95.0	511.58
MHR	95.0	2,036.84	95.0	2,036.84	95.0	2,036.84
Converter	95.0	6,241.26	95.0	1,515.79	95.0	3,495.79
Fluid Bed Roaster	95.0	2,034.57	95.0	2,034.57	95.0	2,034.57
6. Citrate System: O_2 Enrichment						
Reverb Furnace	95.0	633.6	95.0	475.2	95.0	554.4
MHR	95.0	1,994.02	95.0	1,994.02	95.0	1,994.02
Converter	95.0	6,241.26	95.0	1,515.79	95.0	3,495.79
Fluid Bed Roaster	95.0	1,991.46	95.0	1,991.46	95.0	1,991.46

C. Acid plant designed for maximum flow to acid plant -- rounded to nearest 1,000 SCFM.

D. Maximum SO_2 emissions from acid plant based on 2,600 ppm (0.26 percent) for single contact acid plant and 650 ppm (0.065 percent for double contact acid plant. Thus, maximum SO_2 emissions will be based on maximum volume to acid plant.

E. SO_2 emissions from the FGD systems are based on a 90 percent efficiency for the system; thus, 10 percent of the sulfur processed in such systems will be released to the atmosphere.

F. The uncontrolled SO_2 emissions represent fugitive emissions based on a sulfur balance for 1,400 TPD concentrate containing 30 percent sulfur:

$$1{,}400 \text{ TPD} \times 0.3 \text{ S} \times \frac{2 \text{ lb } SO_2}{1 \text{ lb S}} = 840 \text{ TPD - } SO_2.$$

Thus, for the two cases:

Case 1:

MHR: 43,000 SCFM at 5.0% SO_2 = 276.43 TPD - SO_2 = 32.91%
RF: 54,000 SCFM at 1.0% SO_2 = 69.43 TPD - SO_2 = 8.26%
Conv.: 82,000 SCFM at 4.5% SO_2 = 474.43 TPD - SO_2 = 56.48%
97.65%

This implies 2.35% fugitive emissions = 19.7 TPD - SO_2.

Case 2:

FBR: 23,600 SCFM at 9.1% SO_2 = 276.12 TPD - SO_2 = 32.88%
RF: 54,000 SCFM at 1.0% SO_2 = 69.43 TPD - SO_2 = 8.26%
Conv.: 82,000 SCFM at 4.5% SO_2 = 474.43 TPD - SO_2 = 56.48%
97.62%

This implies 2.38% fugitive emissions = 20.0 TPD - SO_2.

Additionally, for Case Nos. 17 and 18 the fugitive emissions are added to the uncontrolled reverberatory SO_2 emissions.

G. The total SO_2 in TPD charged to the system is 840 TPD - SO_2.

APPENDIX Y-4

SPECIFIC ASSUMPTIONS FOR ADDITIONAL BLENDING SCENARIOS (TABLE 6-6 IN TEXT)

All assumptions considered for Table 5-4 are applicable here with the additional assumption that:

For Numbers 51-58, the strategy was to blend all offgas streams and bleed a portion off to send to a FGD system. The volume of the bleed-off stream was determined by calculating the amount required to achieve an 8.0 percent SO_2 stream which could be sent to the acid plant. The 8.0 percent SO_2 is usually the maximum that can be processed in an acid plant without adding dilution air; this strategy results in a constant SO_2 concentrated stream of reduced volume.

The following equations were used:

For MgO = 10% SO_2 at $X = 0.1X$ where X = concentrated SO_2 volume of FGD system

$$Y\ (Z)\ \frac{.9}{.1} = X$$

Y = volume of bleed stream to FGD

F = volume of initial blended stream

$$0.08 = \frac{(F - Y)\ Z + 0.1\ X}{(F - Y) + X}$$

Z = percent SO_2 of initial blended stream

For Citrate: 95% SO_2 at $X = 0.95\ X$

where X, Y, F, and Z are the same as above.

$$Y\ (Z)\ \frac{.90}{.95} = X$$

$$0.08 = \frac{(F - Y)\ (Z) + .95\ X}{(F - Y) + X}$$

These equations assume that the volumes off the FGD systems are constant (95 percent SO_2 for citrate and 10 percent SO_2 for MgO) and that a 90 percent efficiency is realized.

SULFURIC ACID PLANT COST ANALYSIS

Capital Cost Analysis

Detailed cost analyses were prepared for two different acid plant gas handling capacities. The analyses were made for double contact/double absorption (DC/DA) acid plants handling 85,000 and 50,000 scfm of gas at 4.25 percent SO_2. From these costs, Figure 1 was generated for DC/DA acid plants.

Annual Operating Costs

Figure 2 indicates the annual operating costs for DC/DA acid plants. When calculating operating costs for two acid plants, i.e., when the feed volume is greater than about 110,000 scfm, annual operating costs will not be double the value obtained from the figure; rather, operating labor costs for the second plant must be subtracted since it is considered that the same crew can operate two side-by-side plants as one.

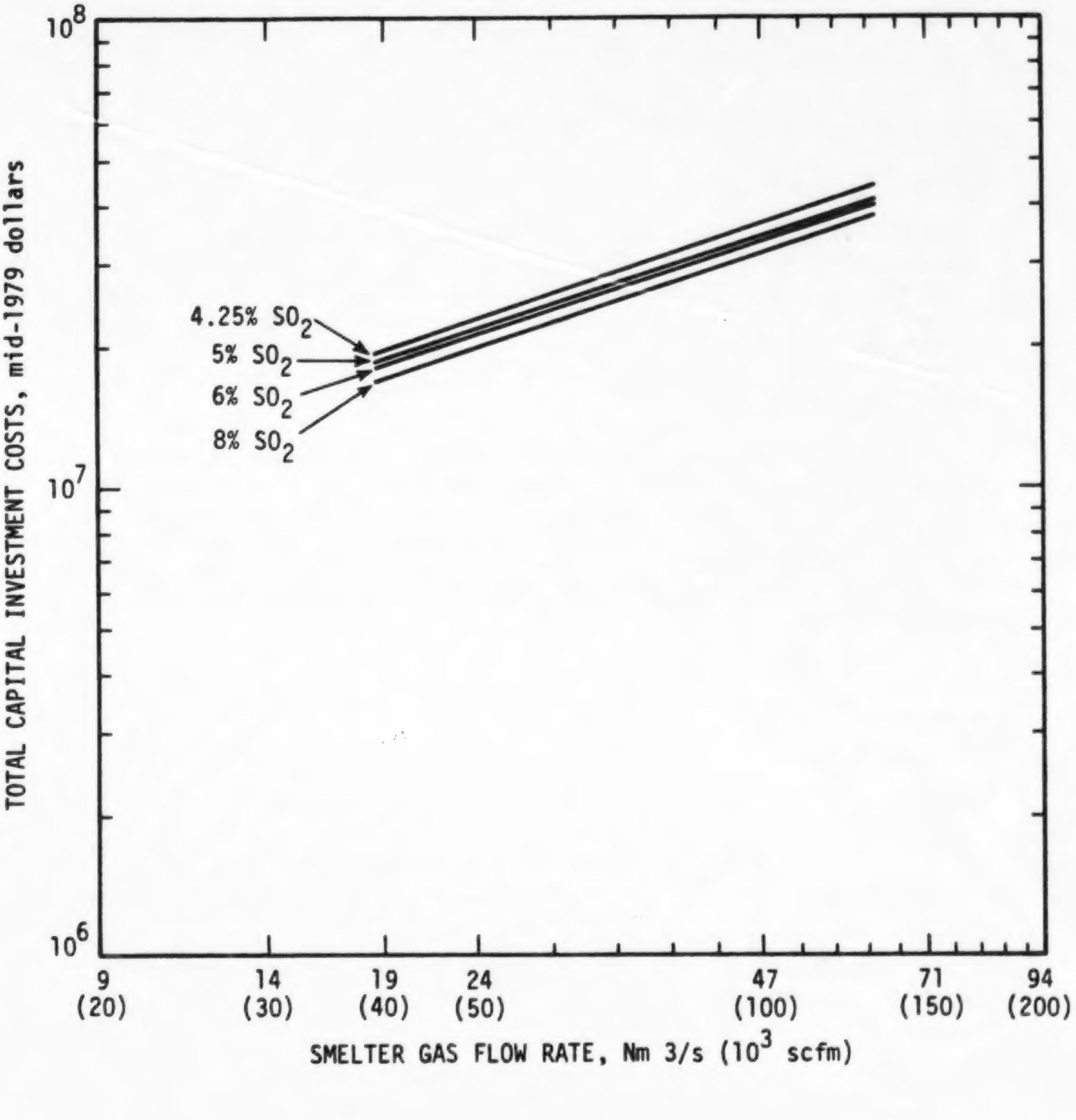

Figure 1. Cost Metallurgical (Copper Smelting) Sulfuric Acid Plants at Different SO_2 Gases and Flows (SCFM), Double Contact (DC/DA)

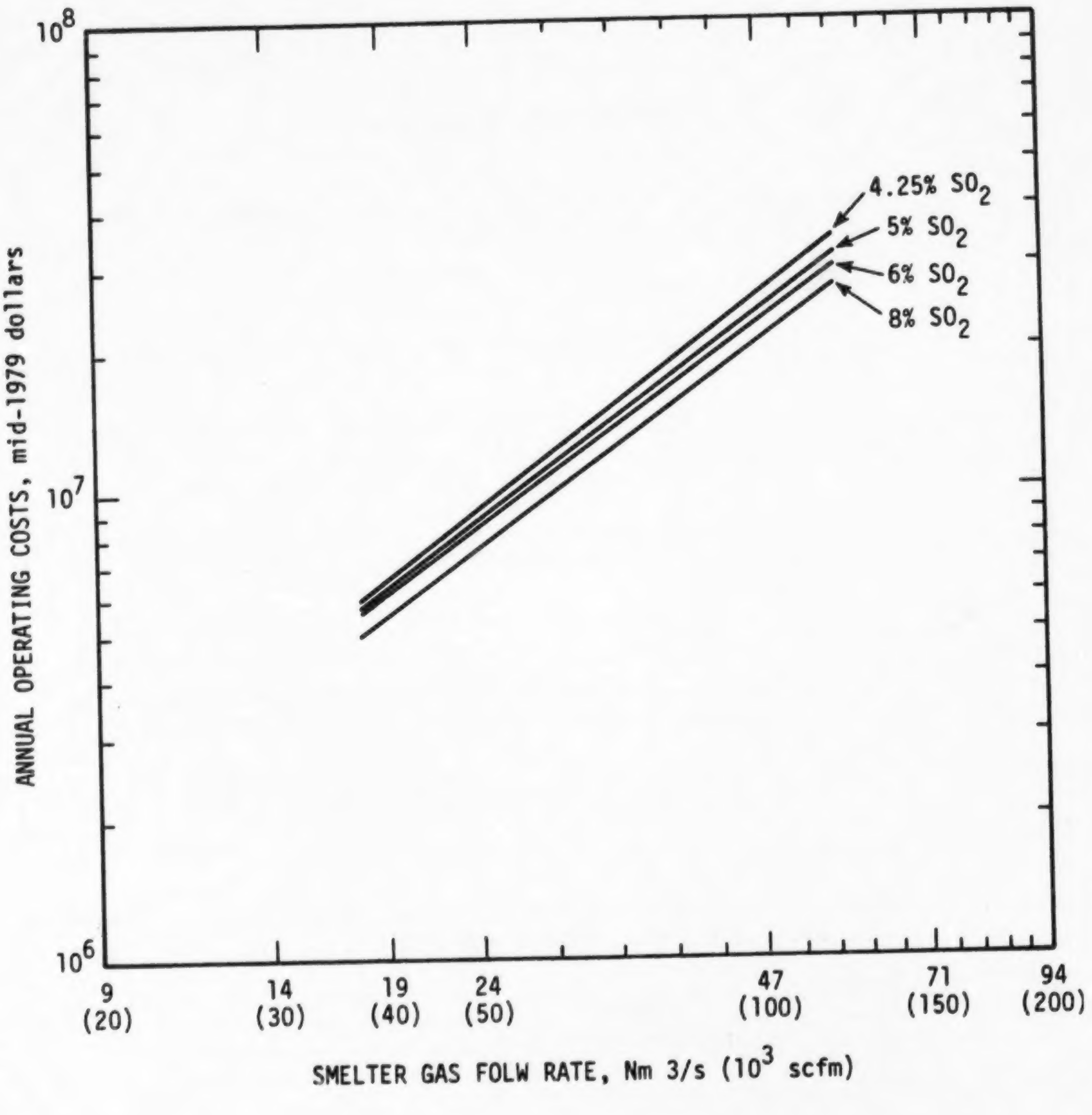

Figure 2. Annual Operating Costs for Sulfuric Acid Plants -- Double Contact Acid Plants (DC/DA)

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